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Near-infrared spectrum and rotational predissociation dynamics of the He–HF complex from an \textit{ab initio} symmetry-adapted perturbation theory potential

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Starting from an \textit{ab initio} symmetry-adapted perturbation theory potential energy surface we have performed converged variational and close-coupling calculations of the bound rovibrational states and of the positions and widths of rotationally predissociating resonances of HeHF and HeDF van der Waals complexes. The energy levels were used to compute transition frequencies in the near-infrared spectra of these complexes corresponding to the simultaneous excitation of vibration and internal rotation in the HF(DF) subunit in the complex. The computed transition energies and other model independent characteristics of the near-infrared spectra are in excellent agreement with the results of high-resolution measurements of Lovejoy and Nesbitt [C. M. Lovejoy and D. J. Nesbitt, J. Chem. Phys. 93, 5387 (1990)]. In particular, the \textit{ab initio} potential predicts dissociation energies of 7.38 and 7.50 cm\textsuperscript{-1} for HeHF and HeDF, respectively, in very good agreement with the Lovejoy and Nesbitt results of 7.35 and 7.52 cm\textsuperscript{-1}. The agreement of the observed and calculated linewidths is less satisfactory. We have found, however, that the linewidths are very sensitive to the accuracy of the short-range contribution to the $V_j(r,R)$ term in the anisotropic expansion of the potential. By simple scaling of the latter component we have obtained linewidths in very good agreement with the experimental results. We have also found that this scaling introduces a very small (2\%) change in the total potential around the van der Waals minimum.

I. INTRODUCTION

Knowledge of intermolecular potential energy surfaces (IPS) is crucial for understanding the properties of molecular gases, liquids, and solids. Several of these properties, such as vibrational and rotational transitions in the gas and liquid phases and phonon frequencies in solids, have been used to test and refine \textit{ab initio} potentials (see Refs. 1–3 for recent reviews). However, the data which depend most sensitively on the details of the anisotropic intermolecular potentials in the physically important region of the van der Waals minimum are the spectra of van der Waals molecules. Since for simple systems nearly exact dynamical calculations of the rovibrational energy levels can be performed at present, any discrepancy between the observed and calculated spectra can be attributed to some deficiencies of the intermolecular potential.

The determination of the potential energy surfaces from the experimental data is highly nontrivial, and has so far been possible only for a few favorable cases (see, e.g., Refs. 4–8). Moreover, the arbitrariness in choosing both the analytical form and the variable parameters of the empirical potentials raises the question about the relation of various terms in those potentials to the physical reality. Indeed, some components of the interaction energy may be completely unrealistic, with compensating contributions providing nevertheless a satisfactory overall potential (see, e.g., Refs. 9–12).

On the other hand, complete potential energy surfaces for van der Waals molecules from \textit{ab initio} calculations are seldom available. This is due, in part, to the enormous difficulty of an accurate \textit{ab initio} description of the van der Waals bonding. Indeed, accurate calculations of IPS require the use of large basis sets with high angular momentum functions, carefully optimized for multipole properties of monomers, and the inclusion of high-order correlation effects. Moreover, only a few \textit{ab initio} potentials have been checked by exposing them to the severe test of computing the observed (high-resolution) spectra of these van der Waals molecules. The ones that have been tested include the potential energy surfaces for the N\textsubscript{2} dimer,\textsuperscript{13–16} NeHF,\textsuperscript{17,18} H\textsubscript{2}HF,\textsuperscript{19,20} and ArNH\textsubscript{3}.\textsuperscript{21–24}

Recently, a new, physically motivated theoretical method of calculating IPS for van der Waals molecules has been developed.\textsuperscript{25–35} This method, referred to as the many-body symmetry-adapted perturbation theory (SAPT), has been applied with success to determine interaction potentials for the HeF\textsuperscript{+}, (Ref. 12), HeK\textsuperscript{+} (Ref. 36), and ArH\textsubscript{2} (Ref. 37) systems. The potential energy curve for the HeK\textsuperscript{+} (Ref. 36) molecular ion was in very good agreement with the mobility derived potential of Viehland (Ref. 7), and reproduced accurately all available experimental transport coefficients of the K\textsuperscript{+} ions in the He gas. The three-dimensional potential energy surface for the ArH\textsubscript{2} system\textsuperscript{37} was in excellent agreement with the empirical potential of LeRoy and Hutson.\textsuperscript{9} Recent calculation of the rovibrational levels of ArH\textsubscript{2} and ArD\textsubscript{2} complexes\textsuperscript{38} using the \textit{ab initio} potential\textsuperscript{37} proves the high accuracy of this potential energy surface since the resulting infrared transitions agree with the available experimental data with an error of the order of 0.1 cm\textsuperscript{-1}. A similar study of the ArHF complex will be presented in a forthcoming paper.\textsuperscript{39}
Recently, Lovejoy and Nesbitt\textsuperscript{40} reported the first spectroscopic study of the near-infrared vibration-rotation spectra corresponding to the simultaneous excitation of the vibration and rotation of HF within the HeHF complex. By correcting the long-range dispersion term in the \textit{ab initio} potential of Ref. 41 they were able to obtain an anisotropic potential energy surface which reproduced all spectroscopic data available for HeHF. In the preceding paper\textsuperscript{42} we reported a potential energy surface for the HeHF complex calculated using the many-body SAPT theory. The intermolecular potential has been represented as an expansion in terms of Legendre polynomials. Each contribution to the interaction energy has been fitted to an analytical form with adjustable, and physically interpretable, parameters. Further improvement of the important dispersion term has been achieved by the computation of high-quality long-range dispersion coefficients at the same level of the theory\textsuperscript{43-45} in a large \textit{spdfg} basis set.

Our potential energy surface is in very good agreement with the empirical potential of Lovejoy and Nesbitt.\textsuperscript{40} In particular, the anisotropy of the two potential energy surfaces compares very well, although around the "T-shape" geometries the two surfaces appear to be slightly shifted and the agreement is somewhat worse. Since various experimentally observed spectroscopic parameters are sensitive to different anisotropic terms in the Legendre expansion of the potential, it is interesting to check their correctness by computing the near-infrared spectrum and linewidths and compare them with the results of high-resolution measurements.\textsuperscript{40}

In the present paper we describe the calculation of bound and resonance states of the HeHF complex using the \textit{ab initio} SAPT potential.\textsuperscript{52} The results of variational and scattering calculations will be used to characterize the near-infrared spectrum of the complex and to study the rotational predissociation dynamics. This study will allow us to test the correctness of various anisotropic terms in the \textit{ab initio} potential. The paper is organized as follows. In Sec. II we discuss theoretical aspects of the HeHF states involved in the observed near-infrared transitions.\textsuperscript{40} The formalism used to compute bound and resonance states of the complex is briefly outlined in Sec. III, while in Sec. IV we present some details of the numerical procedures. Numerical results are presented and discussed in Sec. V. Finally, in Sec. VI we present conclusions.

II. THEORETICAL ASPECTS

Our IPS for the HeHF complex\textsuperscript{42} is described in the Jacobi coordinates \((r,R,\theta)\), where \(r\) is the HF internuclear (stretching) distance, \(R\) is the distance from the He atom to the center of mass of HF, and \(\theta\) is the angle between the vector pointing from the center of mass of HF to He and the vector pointing from F to H (see Fig. 1). Although for three-body systems the dynamical calculations of rovibrational energy levels are nearly exact, it may be helpful to characterize the calculated states by approximate quantum numbers. First, we note that the HF vibrations can, to a very good approximation (Ref. 46), be decoupled from intermolecular modes due to the high frequency of the HF stretching fundamental (3961.4229 cm\textsuperscript{-1}, Ref. 47). In order to visualize the importance of anisotropic contributions to the intermolecular potential \(V(r,R,\theta)\) we report in Table I the values of the coefficients \(V_l(r,R)\) in the Legendre expansion of the potential

\[
V(r,R,\theta) = \sum_{l=0}^{8} V_l(r,R) P_l(\cos \theta)
\]

(1)

for various \(R\) and fixed \(r\). Although around the van der Waals minimum the interaction energy is dominated by the isotropic term, the leading anisotropic term is still large compared to the rotational constant of HeHF (see Ref. 40 and Sec. V), but small compared with the rotational constant of the free HF monomer. This suggests that the energy levels and infrared transitions in HeHF can be approximately classified using the case \(b\) coupling of Bratoz and Martin (Ref. 48) (see Ref. 49 for a review), i.e., the HF subunit should behave as a hindered rotor.

Choosing the \textit{embedded} reference frame such that the vector \(R\) connecting the HF center of mass with the He atom defines the new \(z\) axis (see Fig. 1), the Hamiltonian describing the nuclear motion can be written as\textsuperscript{40-52}

\[
\hat{H} = b_v \hat{J}^2 - \frac{\hbar^2}{2\mu R} \frac{\partial^2}{\partial R^2} R + \frac{\hat{j}_z^2 + \hat{j}_y^2 - 2 \hat{j}_x \hat{j}_y}{2\mu R^2} + V(r_v,R,\theta),
\]

(2)

![FIG. 1. The body-fixed frame used in the dynamical calculations.](image)

<table>
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<th>(R = 6)</th>
<th>(R = 8)</th>
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<td>-0.038</td>
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<tr>
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</tr>
</tbody>
</table>
where \( \mu^{-1} = m^{-1}_{1e} + (m^{-1}_{1H} + m^{-1}_{1F})^{-1} \) is the reduced mass of the complex, \( b_v \) is the rotational constant corresponding to the \( v \)th vibrational state of HF, and \( r_v \) is the average bond length of the HF \( v \)th vibrational state. In Eq. (2) we explicitly assumed that the HF subunit is treated as a rigid fragment. However, the effects of HF vibrations are implicitly taken into account via the dependence of the monomer rotational constant \( b_v \) and of the potential \( V(r_v, R, \theta) \) on the HF subunit stretching quantum number \( v \). In Ref. 46 it was shown that this approximation introduces a very small error compared to a full three-dimensional calculation. The angular momentum operator of the HF subunit (acting on the variables \( \theta \) and \( \phi \)) is designated by \( \mathbf{j} \), and \( \mathbf{J} \) is the total angular momentum operator. Note that the present coordinate system corresponds to the so-called “two-thirds body-fixed” system of Ref. 52. Therefore, the angular momentum operators \( \mathbf{j} \) and \( \mathbf{J} \) do not commute, so the third term in Eq. (2) cannot be factorized.

The only rigorously conserved quantum numbers are the total angular momentum \( J \) and the spectroscopic parity \( p \). [The spectroscopic parity \( p \) is related to the conventional parity \( \sigma \) by the relation \( p = \sigma (-1)^b \).] However, the HF rotational quantum number \( j \), and the projection \( K \) of \( \mathbf{J} \) onto the body-fixed intermolecular axis, are nearly conserved. This conservation is only broken by off-diagonal Coriolis interaction.\(^{50-52} \) Indeed, in the limit of the case \( b \) coupling,\(^{48} \) where we assume that both \( j \) and \( K \) are conserved, the wave function describing the nuclear motion in the dimer can be written as

\[
\psi_{JMK}^{JM} = \phi(R) \left[ Y_{J,K}^{\alpha,\beta,\gamma}(\theta, \phi) \right] \mathcal{D}_{JMK}^{JM}(\alpha, \beta, 0) + p Y_{J,-K}^{\alpha,\beta,\gamma}(\theta, \phi) \mathcal{D}_{JMK}^{JM}(\alpha, \beta, 0),
\]

where \( (\beta, \alpha) \) are polar angles of the \( R \) vector in the space-fixed coordinates, \( Y_{J,K}^{\alpha,\beta,\gamma}(\theta, \phi) \) is the spherical harmonic, \( \mathcal{D}_{JMK}^{JM}(\alpha, \beta, \gamma) \) is an element of the Wigner rotation matrix,\(^{53} \) and \( \phi(R) \) is the function describing the radial motion in the dimer. The energy levels of the complex can be obtained from the first-order perturbation theory formula\(^{49} \)

\[
E_{JMK} = \hbar \omega_V + b_v j(j+1) + B [J(J+1) + j(j+1) - 2K^2] + \sum_{l=0}^{\infty} \tilde{V}_l g_l(jK),
\]

where \( \hbar \omega_V \) is the energy corresponding to the stretching vibration of the van der Waals bond, \( B \) is the rotational constant of the complex, \( \tilde{V}_l \) is the average of \( V(r_v, R) \) over radial motions, and \( g_l(jK) \) is the standard Gaunt coefficient. Note that the Gaunt coefficients vanish for odd values of \( l \). This suggests that the energy levels and transition energies are mainly sensitive to even terms in the angular expansion of the intermolecular potential. Since \( K \) is the projection of an angular momentum, states with \( K = 0, \pm 1, \pm 2, ..., \pm J \) will be designated by superscripts \( e \) and \( f \), respectively. For \( K = 0 \) only \( e \) parity states exist. Thus, the first-order perturbation theory formula (4) gives a very simple classification of the rovibrational energy levels in HeHF:

Each monomer rotational level \( j \) is split into \( j+1 \) levels corresponding to any \( J \geq |K| \) with \( K = 0, \pm 1, \pm 2, ..., \pm J \). Note, however, that Eq. (4) neglects the angular-radial coupling and the off-diagonal Coriolis coupling arising from the \( \tilde{J}_1 \mu R^2 \) term in the Hamiltonian (2). The latter term connects states with the same \( J, j, \) and \( p \) with \( |K| \) differing by \( \pm 1 \). The inclusion of the Coriolis interaction introduces further splitting of the states with \( |K| \neq 0 \) (the so-called \( I \) doubling) into states with \( e \) and \( f \) parity labels.

The allowed dipole transitions between the states of the complex can be deduced from an analysis of the expression for the transition intensity \( I[(J''',p'') \rightarrow (J',p')] \). The intensity of a dipole transition from the state \( (J'',p'') \) to the state \( (J',p') \) is proportional to the square of the dipole matrix element between these states,\(^{34} \)

\[
I[(J'',p'') \rightarrow (J',p')] \sim \sum_{M''=-J''}^{J''} \sum_{M'=0}^{J'} \sum_{m=-J'}^{J'} |\langle \Psi_{J'M'm} | \hat{\mu}_m | \Psi_{J'M''m} \rangle |^2,
\]

where \( \Psi_{J'M'm} \) (\( \Psi_{J'M'm} \)) is the exact wave function of the initial (final) state, and \( \hat{\mu}_m \) is the operator of the \( m \)th spherical component of the dipole moment. It follows easily from Eq. (5) that the observed dipole transitions must obey the following rigorous selection rules:

\[
J'' = J', \quad p'' = -p' \tag{6}
\]

or

\[
J'' = J' \pm 1, \quad p'' = p'. \tag{7}
\]

Since the \( K \) quantum number is nearly conserved, an additional approximate selection rule should hold,

\[
K'' - K' = 0, \pm 1. \tag{8}
\]

Thus, the observed bands in the cold HeHF near-infrared spectrum should correspond to the transitions from the bound \( \Sigma \) states of HeHF(\( v = 0 \)) to \( \Sigma^+, \Pi^+, \) and \( \Pi^1 \) states of HeHF(\( v = 1 \)). In view of Eqs. (6) and (7) for \( \Sigma \rightarrow \Sigma^+ \) and \( \Sigma \rightarrow \Pi^+ \) bands, two branches (\( P \) and \( R \)) corresponding to \( J'' = J' + 1 \) and \( J'' = J' - 1 \), respectively, should be observed, while for the \( \Sigma \rightarrow \Pi^1 \) transitions one branch (\( Q \)) should be observed. The schematic diagram of the energy levels and observed near-infrared transitions is depicted in Fig. 2.

It should be noted that due to the small binding energy of the complex, \( D_0 \approx 7 \text{ cm}^{-1} \) (see Ref. 40 and Sec. V), the only truly bound states are those \( e \) levels which lie below the \( j = 0 \) states of the free HF, and the \( f \) levels which lie below the \( j = 1 \) state of HF. Other states are metastable. Two kinds of resonances are observed. The first kind involves the so-called “shape” or “orbiting” resonances which predissociate directly by tunneling through the centrifugal barrier. The second kind arises from the small binding energy \( D_0 \) of the complex compared to the energy of the \( j = 1 \) internal HF rotation. This leads to the formation of the so-called Feshbach or “compound” resonances\(^{35} \) which decay via internal rotational predissociation mechanism: the energy of the \( j = 1 \) rotational excitation is converted into translation energy of the dissociated fragments. Note, that rotational predissocia-
The basis of radial functions is the complete set of \(7\)-adapted basis, Morse functions. 

Note, that the inversion sends into fragments. This process is found to be extremely slow and dissociation of the \(HeHF\) predissociation, which utilizes the HF vibrational energy to quanta. Consequently, the widths of the compound resonances are expected to be mainly sensitive to odd terms in the angular expansion of the interaction potential. Finally, it should be stressed that all states of HeHF \((v=1)\) may undergo internal vibrational predissociation, which utilizes the HF vibrational energy to dissociate the HeHF \((v=0)\) complex into He and HF \((v=0)\) fragments. This process is found to be extremely slow and will be ignored in the present work.

III. METHOD OF CALCULATIONS

A. Bound state calculations

The bound state problem for the Hamiltonian (2) has been solved variationally in the following orthogonality of \(p\)- and \(J\)-adapted basis,

\[ \Phi_{\gamma}^{(M/p)} = R^{-1} \chi_{\alpha}(R)[Y_{j',k'}(\theta,\phi)\Theta_{\alpha k}(\alpha,\beta,0)] 
+ pY_{j,-k}(\theta,\phi)\Theta_{\gamma k}(\alpha,\beta,0)]. \]

[Note, that the inversion sends \(\Phi_{\gamma}^{(M/p)}\) into \(\Phi_{\gamma}^{(M/p)}\).]

The basis of radial functions \(\{\lambda_{\alpha}(R)\}\) is the complete set of Morse functions,

\[ \lambda_{\alpha}(R) = e^{-y/2}y^{(a+1)/2}L_{\gamma}^{a}(y), \]

where

\[ b = \omega_{c}\left(\frac{\mu}{2D_{e}}\right)^{1/2}, \quad A = \frac{4D_{e}}{b}, \quad a = E(A), \]

\(L_{\alpha}^{a}(y)\) denotes the associated Laguerre polynomial, and \(E(A)\) is the integer part of \(A\). The parameters \(R_{e}\), \(\omega_{c}\), and \(D_{e}\) can be associated with the equilibrium position, fundamental frequency, and dissociation energy of a Morse potential. In practice they were treated as variational parameters.

For high values of \(J\) the dimension of the secular problem can become unmanageable. Therefore, in practice it is useful to use a two-step variational procedure. The Hamiltonian (2) can be partitioned as

\[ \hat{H} = \hat{H}_{0} + \hat{H}', \]

where \(\hat{H}_{0}\) is diagonal in the projection \(K\) of \(\hat{J}\) on the body-fixed intermolecular axis,

\[ \hat{H}_{0} = b_{0}j^{2} - \frac{\hbar^{2}}{2\mu R} \partial^{2}R + \frac{\hbar^{2}}{2\mu R^{2}} + V(r_{o},R,\theta), \]

\[ \hat{H}' = -\frac{\hbar}{\mu R^{2}} j_{x}^2 + j_{y}^2, \]

Here \(j_{x}\) and \(j_{y}\), \(i = x, y, z\), denote the components of the angular momentum operators \(\hat{j}\) and \(\hat{J}\), respectively. In order to compute the bound states of the Hamiltonian (2), one can solve the vibrational problem with the blocked Hamiltonian \(\hat{H}_{0}\) and the basis (9). The effect of the Coriolis coupling is then obtained via an additional variational calculation in a truncated basis consisting of eigenstates of \(\hat{H}_{0}\).

B. Calculations of resonance states

Although the bound states of three-body systems can be computed nearly exactly by the use of the variational approach described earlier, the calculations of positions and widths of resonances are much more difficult and may require additional approximations. There are several methods to treat resonances. The stabilization (Ref. 58) or complex scaling (Ref. 59) methods, widely used in electronic structure calculations (see, e.g., Ref. 60 and references therein), have been applied with only moderate success (Refs. 61 and 62). Quantitative basis set approaches based on the \(L^{2}\) discretization of the continuum (Ref. 63–66) or based on the iterative secular equation perturbation theory \(67,68\) could be applied in practice. In some cases, however, the accuracy of these methods may be difficult to control (see Ref. 68 for a discussion). Other basis set techniques \(69\) are even more approximate and may serve only to distinguish between resonance and unbound scattering states.

In principle, the parameters (positions and widths) of resonance states could be determined from the (computed) profiles of the photodissociation cross sections. \(70–73\) However, assuming that the direct photodissociation is negligible, the positions and widths of resonances can be obtained from...
close-coupling scattering calculations. It is well known that in the vicinity of a resonance the energy dependence of the phase shift \( \delta_l(E) \) can be described by the Breit–Wigner function,

\[
\delta_l(E) = \delta_l^0(E) + \tan^{-1}\left(\frac{\Gamma_j}{2(E_j - E)}\right),
\]

where \( \delta_l^0(E) \) is the contribution from the direct scattering, and \( E_j \) and \( \Gamma_j \) are the energy and the width of the resonance, respectively. Note, that Eq. (16) is valid only in the one open channel case (for a generalization to situations of two or more open channels see, e.g., Ref. 74). In practice, the phase shift as a function of energy can be computed by solving the close-coupling scattering equations at a closely spaced grid of energies \( \{E_j\} \) around the estimated location (e.g., from bound state calculations), subject to standard \( S \)-matrix boundary conditions. The position \( E_j \) and the width \( \Gamma_j \) are then obtained by fitting the computed phase shifts \( \{\delta_l(E_j)\} \) to the Breit–Wigner function (16). We assumed that the direct scattering term \( \delta_l^0(E) \) depends very weakly on the energy, and that it can be approximated as quadratic function of energy. We also assumed that the parameters \( E_j \) and \( \Gamma_j \) are independent of the energy, i.e., that the isolated narrow resonance approximation is valid. This is expected to be the case since the resonances observed for HeHF (Ref. 40) are sufficiently narrow and do not overlap with the neighboring ones.

IV. COMPUTATIONAL DETAILS

In Table II we summarize all relevant parameters used in the calculations. We optimized the parameters \( R_e, D_e, \) and \( \omega_v \) of the radial basis functions to yield minimum energy with fixed size of the basis for the \( J = 0 \) state. As observed previously, the energy was rather insensitive to \( D_e \) and \( \omega_v \), and strongly dependent on \( R_e \). The values of the optimized parameters are given in Table II. All bound state calculations were done using the TRIATOM system of codes. The calculations without the off-diagonal Coriolis interaction were done in a basis of 250 functions with \( j_{\text{max}} = 18 \) and \( n_{\text{max}} = 22 \). The basis functions were selected using the energy criterion. First, all diagonal matrix elements of the Hamiltonian were evaluated, and the 250 basis functions corresponding to the lowest values of these matrix elements were selected for the final basis. The basis for the second step of the variational procedure was again chosen using the energy selection criterion. The final calculations including the Coriolis coupling were done in the basis of 100 (for \( J = 2 \) and 150 (for \( J = 3 \)) eigenfunctions of \( \hat{H}_0 \) with the lowest eigenvalues. The convergence of the eigenvalues has been checked by performing calculations in still larger bases. We found that all eigenvalues are converged within \( 10^{-5} \text{ cm}^{-1} \) or better.

The close-coupling scattering equations were solved using the log-derivative algorithm of Mrugala and Secrest, as modified by Manolopoulos. The angular basis included all channels with \( j \) values up to \( j_{\text{max}} = 18 \). The numerical integration utilized a radial interval from \( R_{\text{min}} = 1.8 \text{ Å} \) to \( R_{\text{max}} = 20 \text{ Å} \), and step length \( \Delta R = 0.01 \text{ Å} \). The integration parameters \( R_{\text{min}}, R_{\text{max}}, \) and \( \Delta R \), as well as the number of channels included in the calculation were chosen to yield the positions and widths converged to \( 10^{-6} \text{ cm}^{-1} \) or better. Other relevant parameters used in calculations are summarized in Table II. The close-coupling calculations were done using the MOLSCAT code. The positions of the resonances were first estimated by diagonalizing the Hamiltonian in a \( L^2 \) basis. The phase shift as a function of energy was determined at a closely spaced grid of 100 energies around the estimated location of the resonance. The parameters of the resonance were then obtained by fitting the computed phase shifts to the Breit–Wigner expression (16). The direct scattering term was assumed to depend quadratically on the energy \( E \), although the linear parametrization of the background gave the same results with \( 10^{-4} \text{ cm}^{-1} \) accuracy. The analytical fits to the computed phase shifts were done using the RESFIT program. The quality of these fits can be characterized by the root mean square deviations (rmsd) between the computed and fitted phase shifts. For almost all resonances rmsd were of the order of \( 10^{-6} \) or smaller.

V. NUMERICAL RESULTS AND DISCUSSION

A. HeHF

In Table III we summarize the results of bound and resonance states calculations. As expected, HeHF is a very weakly bound complex. The potential energy surface for HeHF(\( v = 0 \)) supports only five bound states. In addition to the ground rovibrational state (\( J = 0 \)), the only other bound states correspond to the rotationally excited energy levels of the complex. For comparison we included in Table III the energy levels computed using the empirical potential energy surface. The agreement is very good: the energies of bound states agree within \( 0.05 \text{ cm}^{-1} \) or better. In particular, the theoretical dissociation energy \( D_0 = 7.38 \text{ cm}^{-1} \) compares very well with the result obtained using the empirical potential \( D_0 = 7.35 \text{ cm}^{-1} \). Lovejoy and Nesbitt estimated the dissociation energy of HeHF from dynamical calculations on isotropic potentials, which were fitted to reproduce the observed transition energies of the \( \Sigma \rightarrow \Pi' \) band. These potentials yield the dissociation energy \( D_0 = 7.14 \pm 0.1 \text{ cm}^{-1} \). Our isotropic potential for HeHF(\( v = 0 \)) predicts \( D_0 = 7.25 \text{ cm}^{-1} \), almost within the error bars of the empirical result.
experimentally observed $2e$ and $1T'$ states of HeHF($v=1$), and various isotropic potentials were assumed in the Lennard-Jones form with three variable parameters. Therefore, they may not be very accurate to reproduce the potential energy surface for HeHF($v=0$). In addition to the energy levels of the HeHF($v=0$) bound states, also shown in Table III are the computed positions of resonances corresponding to the ground state1 10 -7.380 -7.347
2 -6.608 -6.572
3 -5.085 -5.043
4 -2.861 -2.812
5 -0.040 +0.011
$\Sigma^e$ bend
0 +30.684 +30.725
1 +31.056 +31.124
2 +32.013 +32.109
3 +33.656 +33.776
4 +35.982 +36.124
5 +38.915 +39.071
$\Pi^e$ bend
1 +34.298 +34.508
2 +36.371 +36.565
3 +39.120 +39.294
$\Pi^i$ bend
1 +33.885 +34.112
2 +35.364 +35.592
3 +37.512 +37.736
4 +40.206 +40.371

*Energy levels computed using the empirical potential (Ref. 40).
*Energies relative to HF($v=0, J=0$).
*Energies relative to HF($v=1, J=0$).
*Resonance states determined from close-coupling scattering calculations.
*Bound states relative to HF($v=1, J=1$).
*Obtained from a variational calculation without the $J=1$ function in the basis.

should be noted, however, that in Ref. 40 the isotropic potentials were assumed in the Lennard-Jones form with three variable parameters. Therefore, they may not be very adequate to represent the isotropic part of the potential energy surface for HeHF($v=0$). In addition to the energy levels of the HeHF($v=0$) bound states, also shown in Table III are the computed positions of resonances corresponding to the ground state. The agreement between the results computed using the $ab$ initio and empirical potential energy surfaces is very good: the positions of the $\Sigma^e$ resonances agree within 0.1 cm$^{-1}$, while the positions of the $\Pi^e$ resonances and energies of the $\Pi^i$ states agree within 0.2 cm$^{-1}$.

The energy levels reported in Table III can be used to compute the transition energies corresponding to the experimentally observed $\Sigma \rightarrow \Sigma^e$, $\Sigma \rightarrow \Pi^e$, and $\Sigma \rightarrow \Pi^i$ bands. Since we assumed that the HF vibrations are decoupled from the intermolecular modes, the transition frequencies were computed from the formula

$$\Delta E(J'' \rightarrow J') = E_{J'} - E_{J''} + Q_1 \left( \frac{\omega(J') - \omega(J'')}{2} \right).$$

where $Q_1 \left( \frac{\omega(J') - \omega(J'')}{2} \right) = 3961.4229$ cm$^{-1}$ (Ref. 47) is the frequency of the HF stretching fundamental. The resulting transition energies are given in Table IV. The agreement of theoretical transition frequencies with the results of high-resolution measurements is excellent. Our potential energy surface predicts all infrared transitions with errors smaller than 0.1 cm$^{-1}$. In particular, the band origins $\Delta E(J'' \rightarrow J')$ of the computed and measured near-infrared spectra agree within 0.2% of the difference $\Delta E(J'' \rightarrow J') - Q_1 \left( \frac{\omega(J') - \omega(J'')}{2} \right)$. It follows from Eq. (4) that the transition energies are mainly sensitive to even terms in the Legendre expansion of the potential. The results reported in Table IV show that at least the even terms in our $ab$ initio potential are very accurate. Also shown in Table IV are transition frequencies computed using the empirical potential. In general, both the theoretical and empirical potentials reproduce the experimental data with similar accuracy. It is interesting to note, however, that some transition energies (the $R$ branch of the $\Sigma \rightarrow \Pi^i$ band and the $\Sigma \rightarrow \Pi^i$ band) are reproduced more accurately by the theoretical potential.

The transition frequencies $\Delta E(J'' \rightarrow J')$ are often represented as a power series in $[J(J+1)-K^2]$. 

<table>
<thead>
<tr>
<th>Transition</th>
<th>$J''$</th>
<th>$J'$</th>
<th>$\Delta E(J'' \rightarrow J')$, Observed (Ref. 40)</th>
<th>$\Delta E(J'' \rightarrow J')$, Computed (Ref. 40)</th>
<th>$\Delta^c$</th>
<th>$\Delta^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Sigma \rightarrow \Sigma^e$</td>
<td>0 1</td>
<td>3999.860</td>
<td>3999.953</td>
<td>3999.894</td>
<td>-0.094</td>
<td>-0.059</td>
</tr>
<tr>
<td></td>
<td>1 2</td>
<td>4000.044</td>
<td>4000.137</td>
<td>4000.104</td>
<td>-0.093</td>
<td>-0.003</td>
</tr>
<tr>
<td></td>
<td>2 3</td>
<td>4000.164</td>
<td>4000.251</td>
<td>4000.242</td>
<td>-0.087</td>
<td>-0.009</td>
</tr>
<tr>
<td></td>
<td>3 4</td>
<td>4000.266</td>
<td>4000.345</td>
<td>4000.359</td>
<td>-0.079</td>
<td>+0.014</td>
</tr>
<tr>
<td></td>
<td>4 5</td>
<td>4000.378</td>
<td>4000.449</td>
<td>4000.483</td>
<td>-0.071</td>
<td>+0.034</td>
</tr>
<tr>
<td>$\Sigma \rightarrow \Pi^e$</td>
<td>0 1</td>
<td>4003.102</td>
<td>4003.161</td>
<td>4003.278</td>
<td>-0.059</td>
<td>+0.117</td>
</tr>
<tr>
<td></td>
<td>1 2</td>
<td>4004.402</td>
<td>4004.418</td>
<td>4004.560</td>
<td>-0.016</td>
<td>+0.142</td>
</tr>
<tr>
<td></td>
<td>2 3</td>
<td>4000.806</td>
<td>4000.904</td>
<td>4000.974</td>
<td>-0.098</td>
<td>+0.070</td>
</tr>
<tr>
<td></td>
<td>3 4</td>
<td>4000.655</td>
<td>4000.735</td>
<td>4000.800</td>
<td>-0.080</td>
<td>+0.065</td>
</tr>
<tr>
<td></td>
<td>4 5</td>
<td>4000.583</td>
<td>4000.639</td>
<td>4000.706</td>
<td>-0.056</td>
<td>+0.067</td>
</tr>
<tr>
<td>$\Sigma \rightarrow \Pi^i$</td>
<td>1 1</td>
<td>4001.916</td>
<td>4002.005</td>
<td>4002.107</td>
<td>-0.089</td>
<td>+0.102</td>
</tr>
<tr>
<td></td>
<td>2 2</td>
<td>4001.871</td>
<td>4001.952</td>
<td>4002.058</td>
<td>-0.081</td>
<td>+0.106</td>
</tr>
<tr>
<td></td>
<td>3 3</td>
<td>4001.796</td>
<td>4001.859</td>
<td>4001.971</td>
<td>-0.063</td>
<td>+0.112</td>
</tr>
<tr>
<td></td>
<td>4 4</td>
<td>4001.669</td>
<td>4001.680</td>
<td>4001.783</td>
<td>-0.011</td>
<td>+0.103</td>
</tr>
</tbody>
</table>

*Measured near-infrared transitions, Ref. 40.
*Computed near-infrared transitions from the empirical potential (Ref. 40).
*Absolute error of the transition frequency computed from the $ab$ initio potential (Ref. 42).
*Absolute error of the transition frequency computed from the empirical potential (Ref. 40).
TABLE V. Model-independent characteristics of the HeHF near-infrared spectrum. All parameters are in cm\(^{-1}\). For the explanation of symbols, see the text.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>This work</th>
<th>Reference 40(^a)</th>
<th>Reference 40(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\omega^\prime)</td>
<td>0.389</td>
<td>0.382</td>
<td>0.390</td>
</tr>
<tr>
<td>(\rho^\prime \times 10^3)</td>
<td>0.996</td>
<td>0.973</td>
<td>1.000</td>
</tr>
<tr>
<td>Blueshift (Q(1) - R(0))</td>
<td>0.927</td>
<td>1.016</td>
<td>1.118</td>
</tr>
<tr>
<td>Redshift (R(1) - P(4))</td>
<td>0.406</td>
<td>0.350</td>
<td>0.283</td>
</tr>
<tr>
<td>Redshift (R(1) - R(0))</td>
<td>1.129</td>
<td>1.036</td>
<td>1.095</td>
</tr>
<tr>
<td>Bandwidth (\Sigma' - \Sigma)</td>
<td>0.518</td>
<td>0.496</td>
<td>0.589</td>
</tr>
<tr>
<td>Bandwidth (\Sigma' - \Pi')</td>
<td>1.300</td>
<td>1.257</td>
<td>1.282</td>
</tr>
<tr>
<td>Bandwidth (\Sigma' - \Pi)</td>
<td>0.223</td>
<td>0.265</td>
<td>0.268</td>
</tr>
<tr>
<td>Bandwidth (\Sigma' - \Pi')</td>
<td>0.247</td>
<td>0.325</td>
<td>0.324</td>
</tr>
<tr>
<td>(\Sigma' - \Pi') spacing (\Delta_{\Sigma'\Pi'})</td>
<td>3.242</td>
<td>3.208</td>
<td>3.384</td>
</tr>
<tr>
<td>(\Sigma' - \Pi') spacing (\Delta_{\Sigma'\Pi'})</td>
<td>4.359</td>
<td>4.281</td>
<td>4.456</td>
</tr>
<tr>
<td>i-doubling (\Delta_{\Pi'\Sigma'})</td>
<td>0.413</td>
<td>0.335</td>
<td>0.396</td>
</tr>
<tr>
<td>i-doubling (\Delta_{\Pi'\Sigma'})</td>
<td>1.007</td>
<td>0.754</td>
<td>0.973</td>
</tr>
<tr>
<td>(\Delta_{\Pi'\Sigma'})</td>
<td>1.421</td>
<td>1.366</td>
<td>1.369</td>
</tr>
</tbody>
</table>

\(^a\)Derived from the measured near-infrared transitions, Ref. 40.
\(^b\)Derived from the near-infrared transitions computed using the empirical potential (Ref. 40).
\(^c\)Branch of the \(\Sigma - \Pi'\) band.
\(^d\)Branch of the \(\Sigma - \Pi\) band.
\(^e\)\(\Delta_{\Sigma'\Pi'}(J)\) denotes the difference of the \(\Pi'\) and \(\Sigma'\) energy levels for a given \(J\).
\(^f\)\(\Delta_{\Sigma'\Pi'}(J)\) denotes the difference of the \(\Pi\) and \(\Pi'\) energy levels for a given \(J\).
\(^g\)Computed using the energy levels reported in Table III.
\(^h\)The experimental value of \(\Delta_{\Pi'\Sigma'}\) determined from a combination of frequencies corresponding to the transitions \((R(1), Q(1), P(2), P(3))\).

\[\Delta E(J' \rightarrow J') = \hbar \omega_0 + B'[J'(J' + 1) - K'^2] - D'[J'(J' + 1) - K'^2] + D''[J''(J'' + 1) - K''^2] + \cdots, \tag{18}\]

where \(\hbar \omega_0\) is the vibrational origin and \(B''\) and \(D''\) are the rotational and distortion constants of the initial (final) state, respectively. Following Ref. 40 we determined \(B''\) and \(D''\) from the combination of frequencies corresponding to \((R(0), R(1), P(2),\) and \(P(3))\) transitions of the \(\Sigma - \Pi'\) band.

where \(\hbar \omega_0\) is the vibrational origin and \(B''\) and \(D''\) are the rotational and distortion constants of the initial (final) state, respectively. Following Ref. 40 we determined \(B''\) and \(D''\) from the combination of frequencies corresponding to \((R(0), R(1), P(2),\) and \(P(3))\) transitions of the \(\Sigma - \Pi'\) band.

\[\Delta E(0 \rightarrow 1) - \Delta E(2 \rightarrow 1) = 6B'' - 36D'', \tag{19}\]

\[\Delta E(1 \rightarrow 2) - \Delta E(3 \rightarrow 2) = 10B'' - 140D''. \tag{20}\]

The resulting rotational and distortion constants of 0.3886 cm\(^{-1}\) and 0.996 \(\times 10^{-3}\) cm\(^{-1}\), respectively, are compared in Table V with those derived from the experimental data. Again, the agreement is very good: the theoretical spectrum reproduces \(B''\) and \(D''\) within 2\%, slightly better than the spectrum generated from the empirical potential. Using the rotational and distortion constants one can predict the frequency of the van der Waals stretch in the pseudodiatomic approximation.83

\[\hbar \omega_v = \left(\frac{4B''^3}{D''}\right)^{1/2}. \tag{21}\]

Our values of \(B''\) and \(D''\) give \(\omega_v = 15.35\) cm\(^{-1}\), in good agreement with \(\omega_v\) derived from the experimental values of \(B''\) and \(D''\): 15.14 cm\(^{-1}\). Note, that the zero-point energy of HeHF\((v = 0)\), \(D_v - D_0 = 32.17\) cm\(^{-1}\), is much larger than the estimated zero-point energy for the stretch vibration \(\frac{1}{2} \hbar \omega_v = 7.68\) cm\(^{-1}\). This shows that a large amount of the zero-point energy is associated with the hindered internal rotations of the HF subunit, and suggests that the wells of the van der Waals potential are too narrow to localize the internal rotor wave functions. This result is consistent with the estimate of the vibrationally averaged distance \(\langle R \rangle\) between the He atom and the center of mass of HF:

\[\langle R \rangle = \left(\frac{\hbar^2}{2\mu B''}\right)^{1/2}. \tag{22}\]

Equation (22) gives \(\langle R \rangle = 6.82\) bohr, substantially larger than the equilibrium distance of the HeHF\((v = 0)\) potential \(r_m = 6.18\) bohr.

Other model independent characteristics of the HeHF near-infrared spectrum are reported in Table V and compared with the experimental data. The \(\Sigma - \Pi'\) band is predicted to be blue shifted by 0.927 cm\(^{-1}\) from the \(R(0)\) monomer transition \([R(0) = 4000.9894\) cm\(^{-1}\) (Ref. 40)]. The \(P\) branch of the \(\Sigma - \Pi'\) and the \(\Sigma - \Sigma\) band are, in turn, red shifted by 0.406 and 1.129 cm\(^{-1}\), respectively. These numbers compare reasonably well with the experimental values of 1.016, 0.350, and 1.036 cm\(^{-1}\), respectively. Except for the red shift of the \(\Sigma - \Sigma\) band, the present results are again slightly more accurate than those derived from the spectrum generated using the empirical potential. The widths of the bands are also predicted quite accurately: 0.518, 1.300, 0.223, and 0.247 cm\(^{-1}\) for the \(\Sigma - \Pi'\) branch of the \(2^2\rightarrow 1^2\) band, and for the \(\Sigma - \Pi\) band, respectively, vs 0.496, 1.257, 0.265, and 0.325 cm\(^{-1}\) for the experimentally observed bands. The \(\Sigma - \Pi'\) spacing \(\Delta_{\Sigma\Pi'}(J)\) is also reproduced correctly.

As discussed in Sec. II, the inclusion of the Coriolis interaction is responsible for the splitting of the \(\Pi\) state into \(\Pi'\) and \(\Pi\) components. The \(l\) doubling, i.e., the energy difference between the \(e\) and \(f\) parity levels, \(\Delta_{\Pi}(J)\), can be easily computed using the energy levels from Table III. The values of \(\Delta_{\Pi}(J)\) for \(J = 1\) and 2 are reported in Table V. \(\Delta_{\Pi}(J)\) cannot be deduced from the experimental spectrum. It can be estimated, however, from the following perturbation theory formula:18,84,85

\[\Delta_{\Pi}(J) = \frac{\beta^2 J(J + 1)}{\Delta_{\Sigma\Pi'}(J)}, \tag{23}\]

where \(\beta\) is the fixed portion of the Coriolis matrix element coupling the \(\Sigma\) and \(\Pi\) states, i.e., \((\Pi|H|\Sigma) = \beta \sqrt{J(J + 1)}\). Using the the experimental values of \(\beta\) and \(\Delta_{\Sigma\Pi'}(J)\), we found the experimental \(l\) doubling of the \(J = 1\) states equal to 0.335 cm\(^{-1}\), in fairly good agreement with the theoretical value of 0.413 cm\(^{-1}\). For \(J = 2\) the agreement is less satisfactory, but for higher values of \(J\) both Eq. (23) and the experimental estimate of \(\beta\) are expected to be too crude approximations. Conversely, one can use Eq. (23) to find the values of \(\beta\) from the computed values of \(\Delta_{\Pi}(J)\) and \(\Delta_{\Sigma\Pi'}(J)\). This gives \(\beta = 0.818\) and 0.855 cm\(^{-1}\) for \(J = 1\) and 2, respectively, in reasonable agreement with the experimental estimate of 0.734 cm\(^{-1}\). Let us mention finally that al-
though the \( J \) doubling of the \( \Pi^e \) states for different \( J \) cannot be deduced from the experimental spectrum, the sum \( \Delta \Pi(1) + \Delta \Pi(2) \) can be computed from the combination of frequencies corresponding to \( R(1), Q(1), P(2), \) and \( Q(2) \) transitions of the \( \Sigma - \Pi^e \) and \( \Sigma - \Pi^e \) bands, 

\[
\Delta \Pi(1) + \Delta \Pi(2) = \Delta E(1 \rightarrow 2) - \Delta E(1 \rightarrow 1) + \Delta E(2 \rightarrow 1) - \Delta E(2 \rightarrow 2).
\]

(24)

As shown in Table V, the theoretical spectrum reproduces the experimental value of \( \Delta \Pi(1) + \Delta \Pi(2) \) within 4%.

Thus far, we have discussed the near-infrared spectrum generated using the \textit{ab initio} potential\(^{42} \) and compared various spectroscopic observables with the experimental data.\(^{40} \) As shown in Sec. II, these data are mainly sensitive to even terms in the Legendre expansion of the interaction potential. The results presented earlier clearly support the accuracy of the \textit{ab initio} SAPT potential.\(^{42} \) However, the odd terms are much smaller than the even ones (see Table I). Therefore, their accuracy may be lower without introducing substantial changes into the anisotropy of the potential, at least in the region of the van der Waals minimum. The correctness of the \( P_i(\cos \theta) \) anisotropy can be checked by computing the widths of resonances decaying via an internal rotational predissociation mechanism. Indeed, rotational predissociation lifetimes can be computed from the Fermi golden rule expression\(^5^6 \) which mixes states with \( j=0 \) and \( j=1 \) via the \( V_i(r, R)P_i(\cos \theta) \) term in the Legendre expansion of the potential. Lovejoy and Nesbit\(^{40} \) measured the linewidths of all \( \Sigma \rightarrow \Sigma^e \) and \( \Sigma \rightarrow \Pi^e \) transitions in HeHF. Thus, a direct comparison of the computed and measured widths will be a severe test of the accuracy of the odd terms.

In Table VI we report the widths of the \( \Sigma^e \) and \( \Pi^e \) resonances calculated using the \textit{ab initio} potential.\(^{42} \) The agreement here is less satisfactory: all computed widths are larger than the measured linewidths\(^{40} \) by a factor of 2. This suggests that the small \( P_i(\cos \theta) \) anisotropy of the potential is not correct. To confirm this assumption we computed the widths of the \( \Sigma^e \) and \( \Pi^e \) resonances using the potential in which the (linear) coefficients \( A_1 \) and \( B_1 \) in the analytical representation of the short-range energy \( 1E_{\text{short}}(R) \) were scaled by 0.95. The resulting widths are given in parentheses. The agreement with the measured linewidths is very good: almost all widths computed using the scaled potential agree with the experimental data within the experimental error bars. The new values of \( \Gamma_j \) also compare very well with those computed using the empirical potential.\(^{40} \) It should be noted that this 5% scaling of the short-range term \( 1E_{\text{short}}(R) \) introduces a very small change in the interaction potential. In the repulsive region (\( R=5 \) bohr and \( \theta=0^\circ \)) the scaled potential is \( \sim 4\% \) smaller than the \textit{ab initio} potential, while the depth of the van der Waals well is only 2% lower. It may be interesting to see, however, the effect of this scaling on the anisotropy of the potential in the region of the van der Waals minimum. In Fig. 3 we compare the anisotropies of the \textit{ab initio}, scaled, and empirical potentials. As expected, the largest changes of the order of 2% are observed for \( \theta=0^\circ \) and 180°. For other angles, the scaled potential differs from the \textit{ab initio} one by 1% or even less. This confirms that the overall anisotropy of the \textit{ab initio} potential is correct. Small inaccuracies of the order of 2% may be due to basis set unsaturation of the \( E_{\text{short}} \) component. These results clearly show that the widths of resonances are extremely sensitive to the accuracy of the odd terms. Consequently, quantitative predictions of the rotational predissociation widths are a challenge for \textit{ab initio} calculations. Surprisingly, the scaling of the \( 1E_{\text{short}}(R) \) component does not resolve the discrepancy between the anisotropies of the \textit{ab initio} and empirical potentials around \( \theta=90^\circ \). Let us mention finally that the energy levels and transition frequencies are insensitive to the scaling of the \( 1E_{\text{short}}(R) \) term: the energies of bound states are changed by less than 0.01 cm\(^{-1} \), while the positions of the resonances are changed by \( \sim 0.05 \) cm\(^{-1} \).

It is interesting to note, that although the widths of the \( \Pi^e \) and \( \Sigma^e \) resonances are not correctly reproduced by the \textit{ab initio} potential, the dependence of the ratio of the \( \Sigma^e \) width to the \( \Pi^e \) width shows a correct dependence on \( J \). Using simple perturbation theory arguments one can show\(^{18} \) that this ratio (denoted by \( \kappa \)) should be roughly proportional to \( J(J+1) \),

\[
\kappa \approx C \cdot J(J+1),
\]

(25)

\[\text{FIG. 3. Comparison of the anisotropies of the } \textit{ab initio} (- - - ), \text{ scaled (---), and empirical (solid line) potentials in the region of the van der Waals minimum (} R = 6 \text{ bohr and } \theta = 1.7328 \text{ bohr).}\]

\[\text{TABLE VI. Calculated widths (MHz) of the HeHF resonance states. The widths corresponding to the scaled potential are given in parentheses.}\]

<table>
<thead>
<tr>
<th>( J )</th>
<th>( \Gamma_j ) This work</th>
<th>( \Gamma_j ) Observed (Ref. 40)(^a )</th>
<th>( \Gamma_j )Computed (Ref. 40)(^b )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Sigma^e ) bend</td>
<td>1</td>
<td>7203 (3452)</td>
<td>3020±500</td>
</tr>
<tr>
<td>&amp; 2</td>
<td>5731 (2673)</td>
<td>2830±200</td>
<td>2730</td>
</tr>
<tr>
<td>&amp; 3</td>
<td>4453 (2001)</td>
<td>1640±150</td>
<td>1999</td>
</tr>
<tr>
<td>&amp; 4</td>
<td>3280 (1397)</td>
<td>1260±100</td>
<td>1349</td>
</tr>
<tr>
<td>&amp; 5</td>
<td>2158 (848)</td>
<td>770±100</td>
<td>780</td>
</tr>
<tr>
<td>( \Pi^e ) bend</td>
<td>1</td>
<td>1080 (575)</td>
<td>530±100</td>
</tr>
<tr>
<td>&amp; 2</td>
<td>1773 (928)</td>
<td>890±150</td>
<td>900</td>
</tr>
<tr>
<td>&amp; 3</td>
<td>1930 (993)</td>
<td>1000±400</td>
<td>990</td>
</tr>
</tbody>
</table>

\(^a\)Measured linewidths, Ref. 40.  
\(^b\)Linewidths computed using the empirical potential (Ref. 40).
The results of calculations on the empirical potential (Ref. 40) are presented graphically the dependence of $U_1$ (Ref. 40) shown as solid line, while the experimental curve is represented by dashed curves (—) and (------), respectively. The constant $C$ can be related to the $\lambda$ doubling of the ET potential. These results also show that the widths of the $\Pi'$ resonances are mainly determined by the Coriolis mixing of the $2$ and $\beta$ states, while the widths of the $2^* \Pi'$ resonances are mainly sensitive to the anisotropy of the potential. It is interesting to note that the agreement between $\Pi'$ and $\Pi''$ potentials is within 0.2 and 0.1 cm$^{-1}$, respectively. Table VII contains the results of bound and resonance state calculations. As for HeHF ($\nu=0$), the core potential energy surface for HeDF ($\nu=0$) supports only five bound states: the ground vibrational state and four rotationally excited energy levels. The agreement with the energy levels computed using the empirical potential is again very good: the energies of bound states agree within 0.02 cm$^{-1}$ or better, while the position of the $\Pi'$ resonance and the energies of the bound $\Pi'$ states agree within 0.2 and 0.1 cm$^{-1}$, respectively. The $ab$ initio potential predicts a dissociation threshold of $D_0 = 7.50$ cm$^{-1}$, which compares very well with the result obtained using the empirical potential ($D_0 = 7.52$ cm$^{-1}$).

In Table VIII we report the frequencies of near-infrared transitions in HeDF accompanying the fundamental band of DF. The transition energies were calculated using Eq. (17), where the frequency corresponding to the DF stretching fundamental is $Q_1(0) = 2906.6608$ cm$^{-1}$. The agreement between the computed and measured frequencies is very good: the band origins of the $\Sigma \rightarrow \Pi'$ and $\Sigma \rightarrow \Pi''$ bands agree within 1% and 0.4% of the difference $\Delta E(J'' \rightarrow J'') - Q_1(0)$, respectively. The experimental data are too limited to determine the rotational and distortion constants for the ground state. However, assuming that the distortion constant for the HeDF ground state is the same as for HeHF, one can estimate

\[ V(r,R) = \frac{2l+1}{2} \int_0^\pi V(r,R',\theta') P_l(\cos \theta') \sin \theta \ d\theta, \]

where $(r,R,\theta)$ and $(r,R',\theta')$ are the Jacobi coordinates with respect to the center of mass of DF and HF, respectively. The constant $C$ can be related to the $\lambda$ doubling of the ET potential, $\lambda$ can be easily written in terms of $R$ and $\cos \theta$.

\[ R' = (R^2 + \delta^2 + 2R\delta \cos \theta)^{1/2}, \]

\[ \cos \theta' = \frac{\delta}{R'} + \frac{R}{R'} \cos \theta, \]

where $\delta$ denotes the distance between the centers of mass of HF and DF.

\[ \delta = \frac{m_D}{m_D + m_F} \frac{m_H}{m_H + m_F} r. \]
TABLE VIII. Near-infrared transitions in HeDF (in cm$^{-1}$) accompanying the fundamental band of DF. The frequency corresponding to the DF stretching fundamental is $\Omega(1) = 2906.6608$ cm$^{-1}$.

<table>
<thead>
<tr>
<th>Transition</th>
<th>$J^*$</th>
<th>$J'$</th>
<th>$\Delta E(J^*\rightarrow J')$ This work</th>
<th>$\Delta E(J^*\rightarrow J')$ Observed (Ref. 40)$^a$</th>
<th>$\Delta E(J^*\rightarrow J')$ Computed (Ref. 40)$^b$</th>
<th>$\Delta '^c$</th>
<th>$\Delta _d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Sigma \rightarrow \Pi^+$</td>
<td>0 0</td>
<td>2929.962</td>
<td>2930.145</td>
<td>2930.161</td>
<td>$-0.183$</td>
<td>$+0.016$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2 1</td>
<td>2927.672</td>
<td>2927.876</td>
<td>2927.860</td>
<td>$-0.202$</td>
<td>$-0.016$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 1</td>
<td>2928.897</td>
<td>2928.974</td>
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<td>$-0.077$</td>
<td>$+0.017$</td>
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<td></td>
<td>2 2</td>
<td>2928.837</td>
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<td>2928.938</td>
<td>$-0.075$</td>
<td>$+0.026$</td>
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<td>3 3</td>
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<td>2928.844</td>
<td>$-0.068$</td>
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<td>4 4</td>
<td>2928.567</td>
<td>2928.604</td>
<td>2928.640</td>
<td>$-0.037$</td>
<td>$+$</td>
<td>$+$</td>
</tr>
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</table>

$^a$ Measured near-infrared transitions, Ref. 40.
$^b$ Computed near-infrared transitions from the empirical potential (Ref. 40).
$^c$ Absolute error of the transition frequency computed from the $ab$ initio potential (Ref. 42).
$^d$ Absolute error of the transition frequency computed from the empirical potential (Ref. 40).

The $B''$ from the difference between the frequencies of the $R(0)$ and $P(2)$ transitions. The theoretical spectrum gives the rotational constant of 0.388 cm$^{-1}$, in very good agreement with the experimental value of 0.384 cm$^{-1}$.

Due to the experimental limitations, only the $J = 1 \Pi'$ resonance has been observed. The measured linewidth of this resonance is 400 ± 100 MHz. Our potential gives a value of 55 MHz, a factor of 10 too small. Surprisingly, the scaling of the short-range energy $\varepsilon_{\text{short}}(R)$ only worsens the agreement with the experimental widths: the scaled potential gives the width of 5.3 MHz. The empirical potential$^40$ also does not reproduce this experimental result. The calculated width on this potential is 14 MHz. We found, however, that the scaling of $\varepsilon_{\text{short}}(R)$ by 1.05 gives the width of 272 MHz, almost within the error bars. This scaling would, however, substantially worsen the good agreement for HeHF. Therefore, this lack of agreement for HeDF must be attributed either to some further inaccuracies of the $ab$ initio potential, or to an error in the measurements.

VI. CONCLUSIONS

Using an $ab$ initio SAPT potential energy surface$^42$ we have calculated bound rovibrational states and positions and widths of rotationally predissociating resonances of HeHF and HeDF complexes. As expected, these complexes are very weakly bound. In addition to the ground rovibrational state, the $ab$ initio potential energy surfaces for HeHF and HeDF support only four bound rotationally excited states. The resulting transition frequencies and other model independent characteristics of the near-infrared spectra of these complexes are in quantitative agreement with the results of high-resolution measurements.$^40$ Our $ab$ initio potential energy surface$^42$ produces transition frequencies of comparable quality to those calculated on an empirical potential of Lovejoy and Nesbitt$^{40}$, optimized to reproduce the results of measurements. In particular, the SAPT potential predicts dissociation energies of 7.38 and 7.50 cm$^{-1}$ for HeHF and HeDF, respectively, in very good agreement with the empirical results$^40$ of 7.35 and 7.52 cm$^{-1}$, respectively. The agreement of the observed and calculated linewidths is less satisfactory. However, the linewidths are found to be extremely sensitive to the accuracy of the short-range contribution to the small $V_1(r,R)$ term in the anisotropic expansion of the potential.

By simple scaling of the latter component we have obtained linewidths in very good agreement with the experimental results. We have also found that this scaling introduces a very small 2% change in the potential around the van der Waals minimum. Our present results look very promising for the predictive power of the intermolecular potentials obtained from $ab$ initio SAPT calculations combined with the calculations of high-quality long-range van der Waals coefficients, and suggest that the symmetry-adapted perturbation theory potentials for weakly bound van der Waals complexes achieve spectroscopic accuracy.

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