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Total differential cross sections and differential energy loss spectra for He–C2H2 from an ab initio potential

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State-to-state elastic and rotationally inelastic differential cross sections for He + C2H2 scattering were obtained from an ab initio potential computed by symmetry-adapted perturbation theory (SAPT) by means of converged close-coupling calculations. From these state-resolved data total differential cross sections at £cm = 71.3 meV and energy loss spectra at £cm = 62.0 and 102.9 meV were determined by transformation to the laboratory frame, and accounting for the experimental conditions via a Monte-Carlo averaging procedure. The results are in excellent agreement with experiment [U. Buck et al., J. Chem. Phys. 99, 3494 (1993)], which proves that the SAPT potential is indeed very accurate. © 1997 American Institute of Physics. [S0021-9606(97)01142-2]

I. INTRODUCTION

The most sensitive probes of intermolecular potential energy surfaces (IPSs) are high-resolution spectra of van der Waals molecules and molecular beam scattering data. While the infrared spectra are mainly sensitive to the interaction potential in the region of the van der Waals well,1-4 the scattering experiments yield information about the interaction both in the attractive and repulsive regions.5 The most detailed beam scattering data are provided by state-to-state experiments. However, also total differential cross sections and (state-unresolved) differential energy loss spectra contain useful information about the anisotropy of the interaction, especially about the repulsive wall region.6

In principle the total differential cross sections measurements can be used to extract intermolecular potential energy surfaces. The inversion procedure is well understood for atomic systems,7,8 but the determination of anisotropic potentials remains still nontrivial, and may be highly nonunique. Moreover, since the scattering data probe mainly the repulsive region in the potential, the IPSs derived from these data may be incompatible with spectroscopic information. On the other hand, ab initio potential energy surfaces that maintain good accuracy both in the attractive and repulsive regions are becoming available.9 Since nowadays accurate quantum close coupling calculations have become feasible, theoretical studies of elementary collisional processes based on accurate ab initio potentials and exact description of the quantum dynamics become important for the interpretation of the growing body of experimental data obtained by more and more sophisticated experimental techniques.

Van der Waals complexes containing the acetylene molecule have been object of many molecular beam experiments.10-19 In particular, the He–C2H2 complex has been almost exclusively investigated using scattering techniques.15-19 Danielson et al.15,16 measured total differential cross sections and diffusion coefficients for this system. The cross sections showed pronounced oscillatory structure, suggesting a rather small anisotropy of the potential energy surface. Indeed, the scattering and bulk data could be accurately reproduced by an analytical potential fit with parameters expanded up to and including the second Legendre polynomial $P_2$.16 These results were in a sharp contrast to results obtained for the He–CO2 complex.20,21 The differential scattering data for the latter system showed a pronounced rotational rainbow, suggesting a large anisotropy in the interaction mainly due to the linear extension of the CO2 molecule.

Recently, Schlemmer,17 Faubel,18 and Buck et al.19 reported total differential cross sections and differential energy loss spectra for the He–C2H2 complex at various collision energies. While the total differential cross sections could be successfully reproduced by the potential of Danielson et al.,16 this potential failed to reproduce the measured differential energy loss spectra, especially at larger collision energies.17-19 Schlemmer,17 Faubel,18 and Buck et al.19 demonstrated that the energy loss spectra are much better reproduced by a potential revealing a spindle-shaped contour22 in the repulsive region rather than the more usual ellipsoidal shape. This suggests that the anisotropy of the scattering potential of Ref. 16 is not entirely correct, at least in the repul-
sive wall region. Recently, Bemish and Miller\textsuperscript{23} measured the near-infrared spectrum of the He–C$_2$H$_2$ molecule corresponding to the simultaneous excitation of the asymmetric stretch vibration and hindered rotation of the C$_2$H$_2$ monomer within the complex. The experimental spectrum could not be successfully assigned\textsuperscript{24} by the use of the potential derived from scattering and bulk data.\textsuperscript{16}

In a recent article, we reported an intermolecular potential energy surface for the He–C$_2$H$_2$ complex\textsuperscript{25} computed using the symmetry-adapted perturbation theory (SAPT).\textsuperscript{9,26–31} Each contribution to the interaction energy was fitted to an analytical form with physically interpretable parameters. This potential was shown\textsuperscript{25} to reproduce all major features of the recorded near-infrared spectrum.\textsuperscript{23} These results suggested that the anisotropy of the SAPT potential for this system is correct, at least in the potential well region. Since experimental total differential cross sections and differential energy loss spectra are available for this system as well, one can use these data to further test the accuracy of the \textit{ab initio} SAPT potential.

The concept of spindle-shaped potentials was introduced into the field of molecular physics by Kihara and co-workers\textsuperscript{22} to determine orientation dependent Lennard-Jones intermolecular potentials, that reproduce the observed second virial coefficients of molecular gases. Nowadays, more advanced models are used to describe interactions between molecules. As a matter of fact, both the perturbational\textsuperscript{9} and supermolecule\textsuperscript{32} approaches interpret the interaction energies in terms of four fundamental components: electrostatics, exchange, induction, and dispersion, as defined by the symmetry-adapted perturbation theory. Since for He–C$_2$H$_2$ a spindle-shaped potential was necessary to reproduce the observed differential energy loss spectra,\textsuperscript{17–19} it is interesting to see to what extent an \textit{ab initio} potential—computed using a high-level treatment of the electron correlation effects—reveals spindle-shaped contours in the repulsive region. If there are any, our \textit{ab initio} results will tell us which physical contributions are responsible for them.

In this article we report the results of exact close coupling (CC) calculations of differential cross sections for He–C$_2$H$_2$ at collision energies of $E_{\text{cm}}$=62.0, 71.3, and 102.9 meV. These calculations are based on our recent potential.\textsuperscript{25} The total differential cross sections at $E_{\text{cm}}$=71.3 meV are compared with the recent experimental results,\textsuperscript{19} while the state-to-state differential cross sections at $E_{\text{cm}}$= 62.0 and 102.9 meV are used to generate the (state-unresolved) energy loss spectra. The latter are again compared with the results of measurements.\textsuperscript{19} The plan of this article is as follows: In Sec. II we briefly describe the formalism used to generate theoretical differential cross sections. In Sec. III numerical results are presented and compared with the measured data. Finally, in Sec. IV we present conclusions.

### II. OUTLINE OF CLOSE COUPLING SCATTERING CALCULATIONS

The coordinate system used in the CC method is a space-fixed frame\textsuperscript{33} The wave function $\Psi_{E,\mu}(R,\hat{r},\hat{R})$ for an atom—rigid linear molecule system corresponding to the total energy $E$, total angular momentum $J$, its projection $M$ on the space-fixed $z$ axis, and parity $\mu$ can be written as an expansion,

$$\Psi_{E,\mu}(R,\hat{r},\hat{R}) = \sum_{J,M} \chi_{j,J}^\mu(R)[Y_j^\mu(\hat{r}) \otimes Y_j^\mu(\hat{R})]_M,$$

where $\hat{r}$ specifies the orientation of the molecule and $\hat{R}$ stands for the polar angles of the intermolecular vector $R$, both with respect to the space-fixed frame. The angle between the vector $R$ and the molecular axis is denoted $\gamma$. The angular functions are Clebsch–Gordan coupled products of spherical harmonics $Y_j^m(\hat{r})$ and $Y_j^m(\hat{R})$.

$$[Y_j^\mu(\hat{r}) \otimes Y_j^\mu(\hat{R})]_M = \sum_{m_1,m_j} \langle jm_1; lm_j|JM \rangle Y_{m_1}(\hat{R}) Y_{m_j}(\hat{r}),$$

where $\langle jm_1; lm_j|JM \rangle$ denotes the standard Clebsch–Gordan coefficient.\textsuperscript{34} The radial functions $\chi_{j,J}^\mu(R)$ are solutions of the system of coupled differential equations (close-coupling equations).

The angular basis of Eq. (2) is adapted to the permutation inversion group $P(I(C_3v))$ (Ref. 35). In other words, the scattering states with even and odd $j$ correspond to states of \textit{para} and \textit{ortho} acetylene in its ground vibrational state, respectively. The asymptotic form of the functions $\chi_{j,J}^\mu(R)$ determines the $S$ matrix elements $S_{j,j'}^{\mu\mu}$. These in turn define the state-to-state differential cross section by the usual expression (see, e.g., Ref. 36).

The close-coupling scattering equations were solved using the hybrid integrator of Alexander.\textsuperscript{37} The log-derivative algorithm of Mrugala and Secrest\textsuperscript{38} was used to propagate from $R_{\text{min}}$ to $R_{\text{end}} = 11.0$ bohr with a constant step of $\Delta R = 0.08$ bohr, and the Airy propagator was used to propagate from $R_{\text{end}}$ to $R_{\text{max}}$. The starting point of the integration $R_{\text{min}}$ was fixed at 4.5, 4.5, and 4.25 bohr for collision energies of 62.0, 71.3, and 102.9 meV, respectively. The corresponding end points were 80.0 bohr for all three collision energies. For $E_{\text{cm}}$=62.0 and 71.3 meV the angular basis included all channels with $j$ values up to and including $J_{\text{max}}$ = 24 and 25 for \textit{para} and \textit{ortho} acetylene, respectively, while for $E_{\text{cm}}$ = 102.9 meV $J_{\text{max}}$ was fixed at 30 and 31 for \textit{para} and \textit{ortho} species, respectively. The number of partial wave components in the calculations of the cross sections was fixed at $J_{\text{max}}=160$. The integration parameters ($R_{\text{min}}$, $R_{\text{end}}$, $R_{\text{max}}$, and $\Delta R$), the number of channels included in the calculation, as well as the number of partial wave components $J_{\text{max}}$ were chosen to yield the state-to-state cross sections converged to 1% at worst. The rotational constant of the C$_2$H$_2$ molecule is $b = 1.176 642$ cm$^{-1}$.\textsuperscript{39} All calculations were performed with the HIBRIDON system of codes.\textsuperscript{40}

### III. NUMERICAL RESULTS AND DISCUSSION

#### A. Total differential cross sections

Experimental data for the total (i.e., summed over all inelastic and elastic channels) differential cross sections of
He + C₂H₂ are given in Fig. 1 for the collision energy of $E_{\text{cm}} = 71.3$ meV. In order to enable comparison with experiment, the calculated data were averaged over the angular and velocity distributions of the two beams, and were corrected for the energy response and physical size of the detector. Furthermore, they were transformed from the center-of-mass (c.m.) to the laboratory (lab) frame. The result is displayed in Fig. 1. The agreement between theoretical and experimental data is nearly perfect. Both the positions and the amplitudes of the diffraction oscillations are reproduced by the calculations in all detail, which indicates that both the onset of the repulsive wall $R_0$ and the anisotropy of the minimum distance $R_m(\gamma)$ of the calculated potential surface are realistic.

B. Energy loss spectra

The second set of observables, the differential energy loss spectra, are essentially sensitive to the anisotropy of the interaction potential. They are measured with high angular, but low energy, resolution and thus, contain information that makes it possible to distinguish between forward and backward scattering. That is, the spectra discriminate between attractive and repulsive forces at the expense of the state selectivity. The experiment of Ref. 19, however, was conducted with C₂H₂ as primary beam and He as secondary beam. This leads to a reduction of the angular resolution, since the c.m. angular range of 180° is squeezed to 15° and 23° for the two collision energies $E_{\text{cm}} = 62.0$ and 102.9 meV, respectively. In addition, the Newton diagram is double-valued, so that the measured time-of-flight (TOF) spectra consist generally of a fast and a slow peak which correspond to one lab angle but two different c.m. angles. The results for different lab angles $\Theta$ and the two energies are shown in Figs. 2 and 3, respectively. In both cases the two peaks coalesce into one when the limiting scattering angle is approached, which occurs at 14° and 21.5° for the two respective energies. The c.m. angular range covers 60°–180°. This means that mainly backward scattered particles were measured which probe the repulsive part of the potential.

A complicated averaging procedure is needed to compare these data with the computational results. The details of this procedure were described in Ref. 41. The intensity of the TOF spectrum at the lab angle $\Theta$ is given by

$$I(t, \Theta) = \sum_{i=1,2} \sum_{-f} p_i \frac{d\sigma}{d\omega}_{\text{if}} (\bar{g}, \bar{\theta}) f(\Delta E_{\text{if}}, \Theta, t),$$

where $p_i$ is the relative initial state population and $(d\sigma/d\omega)_{\text{if}}$ is the c.m. differential cross section for a single rotational transition $i \rightarrow f$, which depends on the relative velocity $\bar{g}$ and the c.m. scattering angle $\bar{\theta}$. The $\sum$ summation is over the fast and slow contribution mentioned above and the $i \rightarrow f$ summation contains all possible transitions which lead to the energy loss $\Delta E_{\text{if}}$ measured at the flight time $t$. The distribution function $f$ contains all the information concerning the averaging process and the transformation from the c.m. to the lab system. It was calculated by a Monte Carlo (MC) procedure, using as input information the measured angular and velocity distributions of the two beams. The critical region for this averaging process is the limiting angle. At this angle, the Jacobian of the transformation from the c.m. to the lab frame becomes singular. In practice, even the smallest spread in some of the variables leads to a finite intensity in the energy loss spectra. On the other hand, the
Heijmen et al.: Energy loss spectra for He–C\textsubscript{2}H\textsubscript{2}

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**FIG. 3.** Comparison of measured TOF spectra in the lab system at the specified deflection angles and the energy $E_{\text{cm}} = 102.9$ meV with CC calculations based on the potential of Ref. 25. Actual values of this distribution depend critically on very small changes in velocity and position space. Therefore, the calculation had to be performed very accurately, with hardly any approximations.

The initial state distribution in the experiment with 75\% *ortho* C\textsubscript{2}H\textsubscript{2} and 25\% *para* C\textsubscript{2}H\textsubscript{2} was 0.42 for $j = 1$, 0.28 for $j = 3$, 0.05 for $j = 5$, 0.13 for $j = 0$, 0.10 for $j = 2$, and 0.02 for $j = 4$. In the calculation we included therefore the initial states with $j = 1, 3, 0,$ and 2. The final states are determined by the maximal possible energy transfer $\Delta E_{\text{max}}$ at each lab angle. These numbers were listed in Table III of Ref. 19. But also in this case we had to extend this range according to the calculated distribution $f$ in Eq. (3) because of the finite resolution.

An example is shown in Fig. 4. Here we compare the calculated energy loss spectrum with the measured one taken at $\Theta = 15^\circ$ and $E_{\text{cm}} = 62$ meV. According to the nominal, possible energy transfer $\Delta E_{\text{max}} = 17$ meV we included all transitions up to $j = 0 \rightarrow 10$ (16.07 meV) and $j = 2 \rightarrow 10$ (15.19 meV). The results in Fig. 4 show an appreciable deviation between measured and calculated values in the region of large energy transfer. If we, however, extend the range to 19.5 meV, a value which was calculated from the averaging procedure, and include the transitions $1 \rightarrow 11$ (18.99 meV) and $2 \rightarrow 12$ (17.53 meV) the agreement between experiment and theory is nearly perfect, as is shown in Fig. 2. This also exemplifies the influence of the transformation near the critical values of the Newton diagram, where two relatively small inelastic cross sections contribute significantly to the energy loss spectra in the lab frame. All other spectra were generated in a similar way.

In general, we can state that the agreement between the calculated and the measured energy loss spectra in Figs. 2 and 3 is very good. This is valid for both collision energies. Not only do we find good agreement for the lab angles $\Theta = 12^\circ - 19^\circ$ at $E_{\text{cm}} = 102.9$ meV, equally good as found in Ref. 19 with an empirical potential, but also at the angles $\Theta = 20^\circ, 21.5^\circ,$ and $23^\circ$ nearly complete agreement is achieved. The same is true for the lower energy $E_{\text{cm}} = 62.0$ meV. Here, the disagreement at the small angles $\Theta = 8^\circ$ and $10^\circ$ found in Ref. 19, which was attributed to the failure of the infinite order sudden (IOS) approximation, is completely removed in the new close coupling calculations. The remaining small discrepancies at the larger deflection angles for $E_{\text{cm}} = 102.9$ meV could be caused by the omitted small contributions starting from the initial states with $j = 4$ and 5.

In any case, the good agreement between measurements and calculations indicates that the *ab initio* potential of Ref. 25 has also the correct anisotropy in the repulsive region.
This anisotropy is larger than that of the empirical potential of Ref. 17. This is demonstrated in Fig. 5 which shows the contour lines $R(\gamma)$ for the energy $V=62$ meV as function of the orientation angle $\gamma$. The $R$-values of the \textit{ab initio} potential are larger in the linear and smaller in the perpendicular approach than those of the spindle-shaped empirical potential leading to a difference $\Delta R$ of 0.83 Å. For comparison, the values for the potential of Ref. 17 are 0.66 and those of Ref. 16 are 0.54 Å. The orientation angle with the steepest slope, which is a measure of the asymmetry of the potential surface, is $37^\circ$ for the \textit{ab initio}, $22^\circ$ for the spindle-shape, and $41^\circ$ for the elliptical shaped potential surfaces. Apparently, the \textit{ab initio} potential, though the potential with the largest anisotropy, does not follow the somewhat artificial shape of a spindle. The expansion in Legendre polynomials shows that indeed terms with $l=2$ and $l=4$ are the largest contributions, so that an elliptical ansatz with $l=2$ only is not sufficient in the repulsive region. The same is true for the spindle-shape ansatz of Ref. 17, since in reality terms up to $l=10$ contribute.

We finally note that in the present case the calculations based on a realistic interaction potential and performed in the exact close coupling formalism reproduce the measured energy loss spectra very well. This gives us confidence that also the complicated averaging procedure, carried out as described earlier, is correct and reliable.

IV. CONCLUSIONS

We calculated state-to-state differential scattering cross sections for He–C$_2$H$_2$ at three collision energies using the exact close coupling formalism. The interaction potential is based on recent calculations applying symmetry-adapted perturbation theory with a high-level treatment of the electron correlation.\textsuperscript{25} The results were summed and averaged for comparison with the measured total differential cross sections at 71.3 meV and differential energy loss spectra taken at 62.0 and 102.9 meV.\textsuperscript{19} All three experimental data sets were reproduced very well indicating, that both the isotropic and the anisotropic part of the near repulsion are realistic. Since this potential is also able to reproduce the major features of the recorded near-infrared spectrum, which are essentially sensitive to the attractive part of the potential, we have one of the very few cases in which detailed scattering and spectroscopic data are completely reproduced by the same potential. While the potential has a global minimum near the linear configuration at $\gamma = 14.16^\circ$ and a local one at $\gamma = 48.82^\circ$ with rather small anisotropy in the attractive region, the shape of the repulsive part is quite anisotropic. At $V=62$ meV, the difference between the linear and perpendicular approach is 0.83 Å and the largest slope is found at $\gamma = 37^\circ$. The characteristic feature of this potential surface is not a special shape but the fact that the anisotropy changes appreciably when going from the attractive to the repulsive part of the potential. This explains also the seemingly contradictory experimental results of scattering experiments. Those experiments which are mainly sensitive to the attractive part of the interaction potential like the damping of the diffraction oscillations in the total differential cross sections\textsuperscript{16} and the rotational energy transfer at small angles and low energy\textsuperscript{17} can be fitted by potentials with small anisotropy. The experimental results presented in Ref. 19 which mainly probe the repulsive part of the interaction require potentials with a relatively large anisotropy.

In order to achieve the results of this article, the interaction potential is of crucial importance. The other ingredients of the data evaluation are the exact close-coupling method for the scattering dynamics and the nearly approximation-free MC procedure for the averaging process.

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Heijmen et al.: Energy loss spectra for He–C2H2

7265

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