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Rotational study of the CH₄–CO complex: Millimeter-wave measurements and *ab initio* calculations

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The rotational spectrum of the van der Waals complex CH₄–CO has been measured with the intracavity OROTRON jet spectrometer in the frequency range of 110–145 GHz. Newly observed and assigned transitions belong to the $K = 2-1$ subband correlating with the rotationless $j_{\text{CH}_4} = 0$ ground state and the $K = 2-1$ and $K = 0-1$ subbands correlating with the $j_{\text{CH}_4} = 2$ excited state of free methane. The (approximate) quantum number K is the projection of the total angular momentum J on the intermolecular axis. The new data were analyzed together with the known millimeter-wave and microwave transitions in order to determine the molecular parameters of the CH₄–CO complex. Accompanying *ab initio* calculations of the intermolecular potential energy surface (PES) of CH₄–CO have been carried out at the explicitly correlated coupled cluster level of theory with single, double, and perturbative triple excitations [CCSD(T)-F12a] and an augmented correlation-consistent triple zeta (aVTZ) basis set. The global minimum of the five-dimensional PES corresponds to an approximately T-shaped structure with the CH₄ face closest to the CO subunit and binding energy $D_e = 177.82 \text{ cm}^{-1}$. The bound rovibrational levels of the CH₄–CO complex were calculated for total angular momentum $J = 0-6$ on this intermolecular potential surface and compared with the experimental results. The calculated dissociation energies D_0 are 91.32, 94.46, and 104.21 cm^{-1} for A ($j_{\text{CH}_4} = 0$), F ($j_{\text{CH}_4} = 1$), and E ($j_{\text{CH}_4} = 2$) nuclear spin modifications of CH₄–CO, respectively. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4933061>]

I. INTRODUCTION

Both methane and carbon monoxide play important roles in atmospheric and combustion chemistry and knowledge about intermolecular interactions involving them can be required in various applications, e.g., interpretation of the spectroscopic data coming from planetary atmospheres and the interstellar gas. High resolution spectroscopy of the van der Waals complex CH₄–CO together with *ab initio* calculation of the intermolecular potential is an efficient tool to reliably elucidate the intermolecular forces because bound states of such complexes are very sensitive to the interaction potential.

The first spectroscopic observations of CH₄–CO have been carried out by Xia *et al.*,¹ who measured rovibrational (C–O stretching $\approx 2143 \text{ cm}^{-1}$) and pure rotational (80–107 GHz) transitions in a pulsed jet supersonic expansion. The spectra included several subbands of infrared (IR) $\nu_{\text{CO}} = 1-0$ transitions, $K = 1-0$, $K = 0-1$, and $K = 2-1$ and one subband of pure rotational millimeter-wave (MMW) transitions, $K = 1-0$ in the $\nu_{\text{CO}} = 0$ ground state. The assigned spectra were relatively simple, closely resembling those of the

rare gas–CO complexes. This was attributed to the fact that all assigned bands originate from the ground internal rotor state with $j_{\text{CH}_4} = 0$. In that work, the authors utilized the free internal rotation model to label the internal rotor states of CH₄–CO, where j_{CH_4} and j_{CO} are quantum numbers for the internal rotations of the CH₄ and CO subunits. The total angular momentum J and its projection K on the intermolecular axis are the other useful quantum numbers.

In free methane, each of the three lowest rotational levels, i.e., $j_{\text{CH}_4} = 0, 1$, and 2 , is associated with a nuclear spin wave function of a distinct A , F , or E symmetry.² This has important effects also on the spectra of the CH₄–CO complex. The internal rotor states that correspond to the excited $j_{\text{CH}_4} = 1$ and 2 monomer rotational levels are metastable and are expected to remain populated in a cold molecular expansion. Rotational transitions originating from these states were observed by Liu and Jäger in subsequent work involving a Fourier transform microwave (FTMW) study of CH₄–CO and its isotopologues.³ In the 4–19 GHz region, they assigned three series of pure rotational transitions of the CH₄–CO complex, two $K = 0-0$, correlating with the $j_{\text{CH}_4} = 0, 1$, and one $K = 1-1$, correlating with the $j_{\text{CH}_4} = 2$ rotational levels of free methane. The isotopic data and the resolved quadrupole hyperfine structure of the observed CH₄–¹³C¹⁷O transitions provided the information

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that the CO subunit makes an angle of about 72° with the intermolecular axis, i.e., that the equilibrium geometry of $\text{CH}_4\text{-CO}$ is essentially T-shaped. It was assumed in the analysis that the O end of CO is closer to CH_4 than the C end.

More recent MMW (116–146 GHz) work⁴ on $\text{CH}_4\text{-CO}$ extended the earlier data on the $K = 1\text{-}0$ rotational transitions¹ originating from the A ($j_{\text{CH}_4} = 0$) state of free methane to higher J -values. The observed spectra showed numerous additional transitions which very likely belong to $\text{CH}_4\text{-CO}$ in the excited F ($j_{\text{CH}_4} = 1$) and E ($j_{\text{CH}_4} = 2$) symmetry states.

The present study provides new assignments of already reported transitions⁴ through additional measurements and *ab initio* calculations. Theoretical studies of $\text{CH}_4\text{-CO}$ were limited to two papers,^{5,6} where the interaction energies were calculated as a function of the intermolecular distance between CH_4 and CO for selected geometries. The present paper presents the first full *ab initio* potential energy surface (PES) of $\text{CH}_4\text{-CO}$ computed at the explicitly correlated coupled cluster level of theory with single, double, and perturbative triple excitations (CCSD(T)-F12a)⁷ and an augmented correlation-consistent triple zeta (aVTZ)⁸ basis set. The bound rotational levels of the $\text{CH}_4\text{-CO}$ complex were calculated for total angular momentum $J = 0\text{-}6$ on this intermolecular potential surface and compared with the experimental results. Our new measurements of $\text{CH}_4\text{-CO}$ provide the first assignments of the $K = 2\text{-}1$ subband correlating with the A ($j_{\text{CH}_4} = 0$) ground state and $K = 2\text{-}1$, $K = 0\text{-}1$ subbands correlating with the E ($j_{\text{CH}_4} = 2$) excited state of free methane.

II. CALCULATION OF THE POTENTIAL ENERGY SURFACE

A. Computational details

The body-fixed (BF) coordinate system used in this part of the work is presented in Fig. 1. The origin of frame 1 is placed on the carbon atom of CH_4 . The hydrogen atoms labeled H' of the methane molecule are located in x_1z_1 plane while the atoms labeled H'' are in the y_1z_1 plane. The intermolecular $\mathbf{R}$ vector connects the centers of mass of CH_4 and CO. The orientation of this vector $\mathbf{R}$ in body-fixed frame 1 is defined by the angles θ_1 and φ_1 . Frame 2, parallel to frame 1, has its origin on the center of mass of CO, and the orientation of the CO axis is described by the angles θ_2 and φ_2 . The monomers CH_4 and CO were considered rigid with geometries corresponding to their ground vibrational state average values: $r_{\text{CH}} = 2.067\text{ }a_0$ ⁹ and $r_{\text{CO}} = 2.137\text{ }a_0$.¹⁰ Thus, the set of five variables $(R, \theta_1, \varphi_1, \theta_2, \varphi_2)$ defines our intermolecular potential.

The five-dimensional (5-D) PES of the $\text{CH}_4\text{-CO}$ complex was obtained at the CCSD(T)-F12a level of theory using the aVTZ basis set. The Basis Set Superposition Error (BSSE) was corrected with the Boys and Bernardi scheme.¹¹ It was previously found^{12–14} that the use of the explicitly correlated coupled cluster method CCSD(T)-F12 allows one to reach the Complete Basis Set (CBS) limit already with medium-sized basis sets. In Fig. 2, we show the convergence of energies obtained using the conventional CCSD(T) method with different basis sets of Dunning and coworkers⁸ to the CBS limit (extrapolation scheme of Peterson *et al.*¹⁵) for

FIG. 1. Coordinate system of the $\text{CH}_4\text{-CO}$ system.

several angular geometries of the $\text{CH}_4\text{-CO}$ complex. The results of CCSD(T)-F12 calculations, both in the “a” and “b” approximations, are also reported in this figure. It is noticeable that the CCSD(T)-F12a and -F12b results are quite similar; however, for the chosen configurations, the CCSD(T)-F12a method with the aVTZ basis set provides results very close to the reference energies corresponding to the CCSD(T)/CBS level.

The CCSD(T)-F12a *ab initio* calculations for the $\text{CH}_4\text{-CO}$ system in its ground electronic state were performed with the Molpro 2010 package.¹⁶ The exponent β in the correlation factor F12 was set to 1.3. The standard auxiliary basis sets and density fitting functions^{17,18} (CABS(OptRI) basis sets) were employed. The size inconsistency was corrected for by subtracting from $V(R, \theta_1, \varphi_1, \theta_2, \varphi_2)$ the asymptotic interaction energy at $R = 1000\text{ }a_0$, which is 10.73 cm^{-1} for all relative orientations. The interaction energy was calculated for a large random grid of angular geometries, which allowed us to estimate the accuracy of the expansion coefficients, see Sec. II B.¹⁹ For each radial grid point R , a total of 3000 geometries were calculated. The intermolecular separation was varied from 4.5 to $30\text{ }a_0$ in 31 radial grid points.

B. Analytical fit

The analytical expansion for an (a)symmetric-top-linear molecule system can be written as

$$V(R, \theta_1, \varphi_1, \theta_2, \varphi_2) = \sum v_{l_1 m_1 l_2 l}(R) t_{l_1 m_1 l_2 l}(\theta_1, \varphi_1, \theta_2, \varphi_2),$$

where the five body-fixed coordinates $(R, \theta_1, \varphi_1, \theta_2, \varphi_2)$ are defined in Fig. 1 and where the expansion functions $t_{l_1 m_1 l_2 l}(\theta_1, \varphi_1, \theta_2, \varphi_2)$ are explicitly given in Phillips *et al.*²⁰ and Valiron *et al.*²¹ The indices l_1 , l_2 , and l refer to the tensor rank of the angle dependence of the CH_4 orientation, the CO orientation, and the intermolecular vector orientation, respectively. As explained by Phillips *et al.*,²⁰ a phased sum over $\pm m_1$ guarantees that the functions are symmetric upon reflection in the target molecule xz -plane. In the rigid-rotor approximation, the tetrahedral symmetry of methane further requires the expansion functions to be invariant under the point group T_d . Explicit expressions of such invariant functions have been given by Heijmen *et al.*²² for the $\text{CH}_4\text{-Ar}$ complex. The tetrahedral symmetry of CH_4 restricts the allowed values of l_1 , e.g., the coefficients with $l_1 = 1, 2, 5$ are strictly zero. For each value of l_1 , the ratio of the expansion coefficients with different

FIG. 2. CH₄-CO interaction energies for different basis sets and methods as a function of the intermolecular distance for selected angular orientations.

m_1 is fixed and defined in Table I of Ref. 22. We note that the normalization of our expansion functions on the four angular coordinates $(\theta_1, \varphi_1, \theta_2, \varphi_2)$ leads to an additional normalization factor of $\sqrt{2}$ for the terms with $l_1 = 4, 6, 8, 10$ and $m_1 = 0$. The expansion coefficients were computed through a least-squares fit on the random grid of angular geometries at each intermolecular separation. We included all anisotropies up to $l_1 = 10$, $l_2 = 10$, and $l = 20$, resulting in 888 basis functions. We then selected only significant terms using a Monte Carlo error estimator (defined in Rist and Faure¹⁹), resulting in a final set of 181 expansion functions with anisotropies up to $l_1 = 10$ (with $m_1 = 0, 2, 4, 6, 8$), $l_2 = 9$, and $l = 14$. The root

mean square residual was found to be lower than 1 cm^{-1} in the long-range and minimum region of the interaction potential ($R > 6.5 a_0$). In this part of the PES, the mean error on the expansion coefficients $v_{l_1 m_1 l_2 l}(R)$ was also found to be smaller than 1 cm^{-1} . A cubic spline radial interpolation of the coefficients $v_{l_1 m_1 l_2 l}(R)$ was finally employed over the whole intermolecular distance range ($R = 4.5\text{--}30 a_0$) and it was smoothly connected to standard extrapolations (exponential and power laws at short and long range, respectively) in order to provide continuous radial expansion coefficients suitable for the bound states calculations presented below. Details on the switch function can be found in Valiron *et al.*,²¹ see their Eq. (10).

FIG. 3. Most stable (global minimum) configuration of $\text{CH}_4\text{-CO}$ complex.

The global minimum of the 5D PES obtained at the CCSD(T)-F12a level of theory corresponds to the structure (Fig. 3) with $\theta_1 = 53.95^\circ$, $\varphi_1 = 0^\circ$, $\theta_2 = 29.84^\circ$, $\varphi_2 = 180^\circ$, and $R = 6.79 a_0$ with binding energy $D_e = 177.82 \text{ cm}^{-1}$. The contribution of the explicit correlation F12a treatment to D_e is 15.23 cm^{-1} ; $D_e^{\text{CCSD(T)}} = 162.59 \text{ cm}^{-1}$ for the geometrical parameters of the global minimum found at the CCSD(T)-F12a/aVTZ level of theory. With the use of the CFOUR package,²³ we have also estimated the effect of a full inclusion of triple excitations on the dissociation energy $D_e^{\text{CCSDT}} = D_e^{\text{CCSD(T)}} + (D_e^{\text{CCSDT}} - D_e^{\text{CCSD(T)}})_{\text{aVDZ}} = 162.05 \text{ cm}^{-1}$. By analogy with the $\text{H}_2\text{-CO}$ complex,²⁴ we suppose that the corrections including quadruples amount to not more than 1 cm^{-1} .

In Fig. 4, we present 2D cuts (with other variables fixed at their equilibrium values corresponding to the global minimum) of the 5D PES of the $\text{CH}_4\text{-CO}$ complex.

III. BOUND STATE CALCULATIONS

A. Theory and computational details

The method used to calculate the rovibrational levels of $\text{CH}_4\text{-CO}$ is described in Ref. 25, where it was applied to $\text{H}_2\text{O-H}_2$. It is based on a general computational method²⁶ developed for weakly bound molecular dimers with large amplitude internal motions, which is similar to a coupled-channel scattering approach. For all details on the form of the Hamiltonian and the basis in BF coordinates, we refer to Refs. 25 and 26. CH_4 is a spherical rotor; we used the experimental ground state values for its rotational constant: $A_0 = B_0 = C_0 = 5.2410356 \text{ cm}^{-1}$ (Ref. 27) and for the rotational constant of CO: $B_0 = 1.92253 \text{ cm}^{-1}$ (Ref. 28). The atomic masses are 1.007825 u for H, 12 for ^{12}C , and 15.994915 u for ^{16}O . The grid in the discrete variable representation (DVR) for the intermolecular center-of-mass

distance R contained 159 equidistant points ranging from $R = 4.5\text{--}20 a_0$. We used a radial basis of 10 functions contracted in the same way as in Ref. 25.

The permutation-inversion (PI) or molecular symmetry² group $G_{24} \equiv T_d(\text{M})$ of $\text{CH}_4\text{-CO}$ is the same as for $\text{CH}_4\text{-Ar}$.^{22,29} The irreducible representations (irreps) of this symmetry group are A_1 , A_2 , E , F_1 , F_2 , with states belonging to the A_1/A_2 irreps having nuclear spin statistical weight 5, states belonging to the E irrep weight 2, and states belonging to the F_1/F_2 irreps weight 3.² Since the nuclear spin functions do not change during the measurements, these symmetries are conserved. The angular basis in our method for bound state calculations of molecular complexes²⁶ usually consists of Clebsch-Gordan coupled products of Wigner D -functions³⁰ for the hindered rotations of the two monomers, multiplied with Wigner D -functions for the overall rotation of the dimer. Here, because CO is linear, its Wigner functions $D^{(j)*}_{mk}$ have $k = 0$ and are spherical harmonics. The adaptation of the basis to the irreps of the symmetry group $T_d(\text{M})$ implies that the Wigner D -functions of CH_4 become tetrahedral rotor functions, which for each value of j are linear combinations of functions $D^{(j)*}_{mk}$ with different values of k and specific coefficients.^{29,31} The expansion of the intermolecular potential described in Sec. II B contains only functions of A_1 symmetry given in Ref. 22; in the angular basis for the wave functions of the complex, we needed functions carrying all irreps A_1 , A_2 , E , F_1 , F_2 of the group $T_d(\text{M})$. Symmetry adapted basis functions for each of these irreps and all values of j were constructed by acting with the projection operators of the group T_d given by Wormer³¹ on a single function $D^{(j)*}_{mk}$. The resulting linear combinations are similar to the tetrahedral harmonics in Ref. 31, but it should be noted that the CH_4 monomer frame used in the present paper, see Fig. 1, is rotated with respect to the frame in Ref. 31 by 45° about the z -axis. Since the number of tetrahedral rotor functions of a given symmetry is considerably smaller than the number of Wigner functions $D^{(j)*}_{mk}$, the use of a symmetry-adapted basis yielded a substantial reduction in computational cost. The angular basis was truncated to internal rotor quantum numbers $j_{\text{CH}_4} \leq 9$ and $j_{\text{CO}} \leq 12$, which was sufficient to converge the bound levels of the complex to better than 0.005 cm^{-1} . The energy differences between levels that determine the frequencies of the allowed transitions are converged much more accurately.

The total angular momentum J and the parity $p = \pm 1$ under inversion are exact quantum numbers. In our analysis

FIG. 4. 2D cuts of our 5D PES of the $\text{CH}_4\text{-CO}$ complex.

of the rovibrational states, we use the spectroscopic parity ϵ , which is related to the inversion parity by $p = \epsilon (-1)^J$. We follow the convention to label states of spectroscopic parity $\epsilon = +1$ by *e* and those with $\epsilon = -1$ by *f*. An approximate quantum number that is important to understand the nature of the rovibrational states is the projection K of the total angular momentum J on the intermolecular axis R . We use the absolute value of K as a label and distinguish the states with $K > 0$ by their parity *e/f*. Calculations have been performed for J values from 0–6, for all irreps.

B. Results

We found that for the states of A_1/A_2 symmetry, the lowest level of $\text{CH}_4\text{-CO}$ has an energy of -91.32 cm^{-1} ; hence, the dissociation energy D_0 is 91.32 cm^{-1} . This ground level has an approximate projection quantum number $K = 0$. For the states of E symmetry, we found the lowest level (with $K = 1$) at -72.76 cm^{-1} , and since the lowest CH_4 monomer level of E symmetry has $j = 2$ and energy 31.45 cm^{-1} , this corresponds to a dissociation energy D_0 of 104.21 cm^{-1} . For the states of F_1/F_2 symmetry, the lowest level (with $K = 0$) has an energy of -83.98 cm^{-1} . The lowest monomer level of this symmetry has $j = 1$ and energy 10.48 cm^{-1} , and therefore, the dissociation energy of this species is $D_0 = 94.46 \text{ cm}^{-1}$. So we note that the E symmetry species with nuclear spin weight 2 is most stable, while the F species with weight 3 is slightly more stable than the A species with weight 5. For all species, a significant fraction of the binding energy $D_e = 177.82 \text{ cm}^{-1}$ goes into the zero-point energy associated with the intermolecular vibrations and internal rotations.

The calculated rotational energy A , E and F -levels of $\text{CH}_4\text{-CO}$ with $K = 0, 1$, and 2 (and 3 for E -levels) and $J \leq 6$ are shown in Figs. 5–7. The zero of energy for each spin modification is simply fixed at the lowest $J = 0$ level of the complex. The relative position of the A , E and F -levels energy scales is determined by the zero-point levels of the complexes given in the preceding paragraph.

Numerical values of calculated energy levels are partly listed in Tables V–VII together with experimental numbers.

FIG. 5. Calculated A -symmetry energy levels and observed transitions of the $\text{CH}_4\text{-CO}$ complex. The zero of energy is fixed at the lowest $J = 0$ level of the $K = 0$ ground state of the complex. The new $K = 2-1$ subbands are shown in bold (green).

FIG. 6. Calculated E -symmetry energy levels and observed transitions of the $\text{CH}_4\text{-CO}$ complex. The zero of energy is fixed at the $J = 0$ (virtual) level of the $K = 1$ ground state. The new $K = 2-1$ and $K = 0-1$ subbands are shown in bold (green).

IV. EXPERIMENTS AND EMPIRICAL ANALYSIS

A. Millimeter-wave experiment

The rotational spectra of the $\text{CH}_4\text{-CO}$ complex in the frequency range of 110–145 GHz were observed using the intracavity OROTRON jet spectrometer. The OROTRON spectrometer³² combined with molecular jet expansion is a quite well-known technique³³ that has been used for the measurements of spectra of weakly bound complexes.

Briefly, the MMW generator OROTRON is placed in a vacuum chamber together with a supersonic jet. The free jet is injected into the OROTRON cavity perpendicularly to its axis. A high Q -factor ($\approx 10^4$) of the cavity results in 100 effective passes of the radiation through the jet. Absorption in the cavity causes changes of the electron current in the collector circuit of the OROTRON and is detected very sensitively by measuring these current changes. A small part of the MMW radiation is taken out from the cavity through coupling openings in a spherical mirror and mixed on a Schottky diode with the radiation of a MW synthesizer for frequency determination. The range of operation of the present OROTRON tube is

FIG. 7. Calculated F -symmetry energy levels and observed transitions of the $\text{CH}_4\text{-CO}$ complex. The zero of energy is fixed at the $J = 0$ level of the $K = 0$ ground state.

TABLE I. Measured transitions for the CH₄-CO complex in the *A*-symmetry ($j_{\text{CH}_4} = 0$) state. New values are given in bold.

Assignment	Frequency (MHz)
$K = 1-0; j_{\text{CO}} = 1-0$	
<i>R</i> (2)	80 103.329 ^a
<i>R</i> (3)	85 748.662 ^a
<i>R</i> (4)	91 246.283 ^a
<i>R</i> (5)	96 595.251 ^a
<i>R</i> (6)	101 795.093 ^a
<i>R</i> (7)	106 845.838 ^a
<i>R</i>(8)	111 747.964
<i>R</i> (9)	116 502.304 ^b
<i>R</i> (10)	121 110.231 ^b
<i>R</i> (11)	125 573.548 ^b
<i>R</i> (12)	129 893.711 ^b
<i>R</i> (13)	134 073.600 ^b
<i>R</i> (14)	138 115.716 ^b
<i>R</i> (16)	145 798.629 ^b
$K = 0-0; j_{\text{CO}} = 0-0$	
<i>R</i> (0)	6 216.0218 ^c
<i>R</i> (1)	12 428.3284 ^c
<i>R</i> (2)	18 633.1900 ^c
$K = 2(e)-1(e); j_{\text{CO}} = 2-1$	
<i>P</i>(8)	137 398.112
<i>P</i>(9)	131 968.792
<i>P</i>(10)	126 631.149
<i>P</i>(11)	121 385.921
<i>P</i>(12)	116 233.228
$K = 2(f)-1(f); j_{\text{CO}} = 2-1$	
<i>P</i>(6)	143 540.620
<i>P</i>(7)	136 282.800
<i>P</i>(8)	128 884.426
<i>P</i>(9)	121 351.093
<i>P</i>(10)	113 688.894

^aMeasured in Ref. 1.^bMeasured in Ref. 4.^cMeasured in Ref. 3.

110–155 GHz with a few small gaps. A detailed description of the spectrometer has been published elsewhere.³³

For the production of complexes, we used a gas mixture of 10% of CH₄ in CO at a backing pressure of 3–4 bars. The gas mixture was adiabatically expanded into the OROTRON cavity through a pulsed pin nozzle (General Valve, Series 9) with an opening diameter of 1 mm operated at a repetition rate of 8–12 Hz.

In addition to the CH₄-CO lines, many transitions of the CO dimer were also observed in the spectrum but most of them

TABLE II. Measured transitions for the CH₄-CO complex in the *E*-symmetry ($j_{\text{CH}_4} = 2$) state. New values are given in bold.

Assignment	Frequency (MHz)
$K = 2-1; j_{\text{CO}} = 0-1$	
<i>R</i>(9)	114 132.272
<i>R</i>(10)	119 443.946
<i>R</i>(11)	124 594.296
<i>R</i>(12)	129 581.587
<i>R</i>(13)	134 407.710
<i>R</i>(14)	139 075.245
$K = 1-1; j_{\text{CO}} = 1-1$	
<i>R</i> (1)	12 255.2698 ^a
<i>R</i> (2)	18 375.2154 ^a
$K = 0-1; j_{\text{CO}} = 2-1$	
<i>R</i>(7)	114 593.534
<i>R</i>(8)	120 733.125

^aMeasured in Ref. 3.

could be easily distinguished from the CH₄-CO lines due to the previous millimeter-wave survey of (CO)₂.³⁴

B. Observed rotational spectrum

The previous IR and MMW^{1,4} and MW³ studies have shown that the spectrum and energy level pattern of CH₄-CO in the *A* internal rotor state ($j_{\text{CH}_4} = 0$) are relatively simple, closely resembling those of the rare gas-CO complexes. The $K = 0$ and $K = 1$ states in the ground $v_{\text{CO}} = 0$ state were detected.^{1,3,4} In the present work for the *A*-symmetry spin modification, we found for the first time the $K = 2$ state by observing the $K = 2-1$ subband, which included five $P_e(8)-P_e(12)$ and five $P_f(6)-P_f(10)$ transitions (see Fig. 5). A similar $K = 2$ state was detected in the IR spectrum of CH₄-CO for the excited $v_{\text{CO}} = 1$ state but not for the ground $v_{\text{CO}} = 0$ state.⁴

Originally, the newly assigned $K = 2-1$ transitions seemed inconsistent with earlier determined $K = 1e/f$ splitting parameters.^{1,4} But then, analysing the new data with the results of the bound state calculations (Section III) that predict the e/f splittings quite accurately, the experimental values of the b and d constants from Refs. 1 and 4 were revised. These constants were obtained earlier on the base of very weak transitions in the IR spectrum¹ and could not be determined independently in the subsequent MMW study,⁴ where only one e -symmetry component of $K = 1$ was observed. Now the energy levels of the $K = 0, 1$ and 2 states of CH₄-CO in the *A* internal rotor state could be determined solely from the MW and MMW data. The frequencies of the measured MW and MMW transitions are listed in Table I.

The E ($j_{\text{CH}_4} = 2$) and F ($j_{\text{CH}_4} = 1$) states of CH₄-CO were less well understood, and only a few $\Delta K = 0$ pure rotational (*end-over-end*) transitions were reported in the MW work.³ Using the results of the bound state calculations for CH₄-CO in the E ($j_{\text{CH}_4} = 2$) state, we have assigned at first six $R(9)-R(14)$ transitions of the $K = 2-1$ subband. Then, carefully searching, we were able to detect another $K = 0-1$ subband and measured two very weak transitions tentatively assigned as $R(7)$ and $R(8)$ lines. All new and previously observed⁶ rotational lines are shown in Fig. 6 and their frequencies are listed in Table II.

Each transition was recorded as a second derivative line shape due to the frequency modulation (25 kHz) and second harmonics detection. Typical linewidths are 400 kHz (full width at half height). Fig. 8 shows an example of a recorded line, namely, the $R(11)$ $K = 2-1$ transition of CH₄-CO in the *E*-state. The accuracy of frequency determination in the new measurements of both CH₄-CO in the *A* ($j_{\text{CH}_4} = 0$) and *E* ($j_{\text{CH}_4} = 2$) states is expected to be about 50 kHz.

No new transitions were assigned for CH₄-CO in the *F* ($j_{\text{CH}_4} = 1$) state (Fig. 7) in addition to previously detected MW lines.³

As shown in both Table I and Table II, the newly detected subbands correlate with $\Delta j_{\text{CO}} = 1$, namely, with free internal rotor quantum number j_{CO} increasing from 0 to 1, 1 to 0, or 1 to 2. Such a free internal rotor interpretation is only partly valid, however, since analysis of the calculated wave functions shows that the j_{CO} values are strongly mixed by the anisotropic interaction potential.

FIG. 8. Recording of the $K=2-1$ $R(11)$ transition of $\text{CH}_4\text{-CO}$ in the E -state.

C. Empirical analysis

The transitions of $\text{CH}_4\text{-CO}$ assigned in this work were fitted together with already known MW³ and MMW data.⁴ In the fitting procedure, the frequencies of the MMW and MW transitions were given weights of 1:100 according to the corresponding measurement accuracies. For $\text{CH}_4\text{-CO}$ in the A -state ($j_{\text{CH}_4} = 0$), we used an empirical energy expression in which each K -stack of levels was represented by a band origin σ plus a power series in $[J(J+1) - K^2]$, and an additional power series in $J(J+1)$ describing the asymmetry splitting,

$$E_{\text{total}} = \sigma + B[J(J+1) - K^2] - D[J(J+1) - K^2]^2 + H[J(J+1) - K^2]^3 + L[J(J+1) - K^2]^4 + \Delta E_K, \quad (1)$$

$$\Delta E_K = \pm 1/2 [bJ(J+1) + d(J(J+1))^2 + h(J(J+1))^3]. \quad (2)$$

In this expression, B is equivalent to $[(B+C)/2]$ and b is equivalent to $[(B-C)/2]$, where B and C are the nearly equal rotational constants of the complex, considered as a conventional near-prolate asymmetric rotor molecule. The asymmetry doubling term ΔE_K is equal to zero for $K=0$ and starts at b for $K=1$, at d for $K=2$, etc.

The results of the fit for $\text{CH}_4\text{-CO}$ in the A -state are given in Table III together with the constants determined in the previous study⁴ and constants obtained from a fit to the *ab initio* levels. For the latter case, the higher order centrifugal distortion parameter H was not considered due to the relatively low J values (≤ 6) of the computed levels. The value of the standard deviation of the measured transitions $\sigma_{\text{fit}} = 61$ kHz is close to our experimental uncertainty. The accurate molecular parameters for the $K=2$ state were determined for the first time. The parameters for the $K=0$ and $K=1$ states agree well with those obtained in Refs. 1 and 4, with one important exception: the d constant of the $K=1$ state has not only a different value but also a different sign. By contrast, the theoretical d constant has the same sign as in previous work,⁴ but its resulting contribution to splitting term (2) agrees remarkably better with the current experimental data, especially at higher J values. As was mentioned in the previous paragraph, the splitting constants b and d were obtained earlier on the base of very weak transitions in the IR spectrum¹ and had to be revised.

The asymmetry doubling term (2) was used only for the $K=1$ and $K=2$ of the A -symmetry states of $\text{CH}_4\text{-CO}$, but not for the E -symmetry states ($j_{\text{CH}_4} = 2$), which were analysed as a symmetric top molecule (expression (1) with $\Delta E_K = 0$). For the close-lying lowest states with $K=0$ and 2 ($j_{\text{CH}_4} = 2$), a Coriolis-type interaction should be introduced, linking levels of the same J value with a term given by

$$W = \beta \{ [J(J+1)] [J(J+1) - 2] \}^{1/2}. \quad (3)$$

Here, β is a Coriolis-type interaction parameter representing a second order interaction.

TABLE III. Molecular parameters for the $\text{CH}_4\text{-CO}$ complex composed of CH_4 in the A -symmetry ($j_{\text{CH}_4} = 0$) state (all values in cm^{-1}).

Present work				
		Experimental	Theoretical ^a	Previous work (Ref. 4)
$K=0$	σ	0.0	0.0	0.0
	B	0.103 682 391(9)	0.103 885 8(2)	0.103 682 390(11)
	D	$5.1552(15) \times 10^{-6}$	$5.172(5) \times 10^{-6}$	$5.1549(12) \times 10^{-6}$
	H	$-8.391(762) \times 10^{-10}$		$-8.576(590) \times 10^{-10}$
$K=1$	σ	2.181 404(3)	2.189 917(2)	2.181 448(10)
	B	0.103 342 97(92)	0.103 496 0(2)	0.103 385 36(970)
	D	$4.0981(530) \times 10^{-6}$	$4.641(5) \times 10^{-6}$	$5.4651(2900) \times 10^{-6}$
	H	$-8.655(641) \times 10^{-10}$		$-8.814(500) \times 10^{-10}$
	b	$3.962 73(202) \times 10^{-3}$	$4.069(3) \times 10^{-3}$	$4.053 09(2100) \times 10^{-3}$
	d	$4.7614(10 557) \times 10^{-7}$	$-3.93(8) \times 10^{-7}$	$-2.2604(5900) \times 10^{-6}$
$K=2$	σ	8.620 989(35)	8.634 928(3)	
	B	0.102 471 63(167)	0.102 514 7(4)	
	D	$3.8364(533) \times 10^{-6}$	$4.662(9) \times 10^{-6}$	
	H	$-1.715(98) \times 10^{-9}$		
	d	$1.2567(1333) \times 10^{-6}$	$0.117(3) \times 10^{-6}$	

^aValues obtained from a fit to the *ab initio* levels.

TABLE IV. Molecular parameters for the CH₄-CO complex composed of CH₄ in the *E*-symmetry ($j_{\text{CH}_4} = 2$) state (all values in cm⁻¹).

Present work				
		Experimental	Theoretical ^a	Previous work (Ref. 4) ^b
$K = 1$	σ	0.0	0.0	0.0
	B	0.102 223 60(142)	0.102 123 7(3)	0.102 232 15
	D	$4.274\,8(1032) \times 10^{-6}$	$4.181(7) \times 10^{-6}$	5.275×10^{-6}
$K = 0$	σ	2.105 311(428)	2.112 981(3)	
	B	0.101 735 72(1596)	0.101 587(2)	
	D	$3.8562(7551) \times 10^{-6}$	$3.66(54) \times 10^{-6}$	
$K = 2$	σ	2.144 800(937)	2.143 235(7)	
	B	0.102 112 71(2030)	0.102 018(2)	
	D	$4.3598(8131) \times 10^{-6}$	$4.00(54) \times 10^{-6}$	
	β	0.001 245(88)	0.001 27(7)	

^aValues obtained from a fit to the *ab initio* levels.^bTwo measured transitions were used to calculate B and D .

The spectroscopic constants obtained for the observed *E*-symmetry states of CH₄-CO are given in Table IV together with the constants determined from the previous study³ and constants obtained from a fit to the *ab initio* levels. Overall, there is good agreement between the parameters for the $K = 1$ state, but their values for the $K = 0$ and $K = 2$ states are determined for the first time. The standard deviation of the fit $\sigma_{\text{fit}} = 103$ kHz for the MMW transitions is larger than our experimental uncertainty, but because of a limited amount of data, especially for the $K = 0$ –1 subband, inclusion of higher order centrifugal distortion constants is not reasonable.

V. DISCUSSION

The calculated positions of the lower states (<15 cm⁻¹) with $K = 0, 1, 2, 3$ of the CH₄-CO complex and linking subbands detected in the present work are shown in Figs. 5–7. According to the bound state calculations, the zeroes of the energy scales for the *E*- and *F*-levels are about 18 and 7 cm⁻¹ higher, respectively, than the zero of the scale for the *A*-levels. It was established in the previous experimental study³ and confirmed here by the *ab initio* calculations that *A*- and *F*-symmetry CH₄-CO have ground states with $K = 0$, while the ground state of *E*-symmetry CH₄-CO is a $K = 1$ state.

For both the *A*- and *E*-symmetry spin modification of CH₄-CO, the three lowest stacks of levels with $K = 0, 1, 2$ are now well characterized by MW and MMW spectroscopy. This is similar to the somewhat analogous case of NH₃-CO, where we recently detected for *ortho*-NH₃-CO (*A*-levels) and *para*-NH₃-CO (*E*-levels), the same K -states linked with the same subbands.¹⁴ The markedly smaller number of $\Delta K = 0$ transitions observed for CH₄-CO is due to lack of a dipole moment of CH₄ in contrast to NH₃.

In Tables V and VI, the experimentally determined energy levels of the CH₄-CO complex are compared with the results of bound state calculations. The theory predicts very accurately the origins of the observed K -stacks as well as pure rotational levels up to the maximum calculated value of $J = 6$. For

the *F*-symmetry spin modification of CH₄-CO, only the lowest stack with $K = 0$ was experimentally detected by MW spectroscopy.³ The experimental and theoretical energy levels for this state demonstrate also very good agreement as shown in Table VII. The slow increase of the (Obs. – Calc.) deviations with increasing total angular momentum J is just due to the poor predictive ability of the experimental

TABLE V. Calculated (*ab initio*) and experimental energy levels of the CH₄-CO complex in the $j_{\text{CH}_4} = 0$ state (*A*-symmetry).

State	J	Calculation (cm ⁻¹)	Observation (cm ⁻¹)	O–C (cm ⁻¹)
$K = 0$ (<i>e</i>)	0	0.000 00	0.000 00	0.000
	1	0.207 75	0.207 34	0.000
	2	0.623 13	0.621 91	–0.001
	3	1.245 88	1.243 44	–0.002
	4	2.075 65	2.071 58	–0.004
	5	3.111 92	3.105 81	–0.006
$K = 1$ (<i>e</i>)	6	4.354 08	4.345 50	–0.009
	1	2.289 34	2.280 78	–0.009
	2	2.695 08	2.686 12	–0.009
	3	3.303 42	3.293 87	–0.010
	4	4.114 05	4.103 71	–0.010
	5	5.126 54	5.115 23	–0.011
$K = 1$ (<i>f</i>)	6	6.340 34	6.327 88	–0.012
	1	2.297 48	2.288 71	–0.009
	2	2.719 48	2.709 91	–0.010
	3	3.352 20	3.341 49	–0.011
	4	4.195 28	4.183 16	–0.012
	5	5.248 26	5.234 54	–0.014
$K = 2$ (<i>e</i>)	6	6.510 56	6.495 15	–0.015
	2	8.839 94	8.825 90	–0.014
	3	9.454 74	9.440 44	–0.014
	4	10.273 95	10.259 32	–0.015
	5	11.297 11	11.282 10	–0.015
	6	12.523 65	12.508 22	–0.015
$K = 2$ (<i>f</i>)	2	8.839 94	8.825 93	–0.014
	3	9.454 75	9.440 59	–0.014
	4	10.273 99	10.259 77	–0.014
	5	11.297 21	11.283 15	–0.014
	6	12.523 86	12.510 33	–0.014

TABLE VI. Calculated (*ab initio*) and experimental energy levels of the CH₄-CO complex in the $j_{\text{CH}_4} = 2$ state (*E*-symmetry).

State	J	Calculation (cm ⁻¹)	Observation (cm ⁻¹)	O-C (cm ⁻¹)
$K = 1$	1	0.102 12	0.102 22	0.000
	2	0.510 51	0.511 01	0.000
	3	1.122 85	1.123 94	-0.001
	4	1.938 84	1.940 71	-0.002
	5	2.958 07	2.960 89	-0.003
	6	4.180 04	4.183 98	-0.004
$K = 0$	0	2.112 99	2.105 31	0.008
	1	2.316 14	2.308 77	0.007
	2	2.722 48	2.715 69	0.007
	3	3.332 02	3.326 09	0.006
	4	4.144 83	4.140 02	0.005
	5	5.160 99	5.157 52	0.003
$K = 2$	6	6.380 59	6.378 65	0.002
	2	2.347 15	2.348 90	-0.002
	3	2.958 60	2.960 91	-0.002
	4	3.772 93	3.775 95	-0.003
	5	4.789 31	4.793 17	-0.004
	6	6.006 73	6.011 55	-0.005

rotational constants.³ Because of the limited amount of data, this $K = 0$ state has been treated as isolated in that work, although a very strong Coriolis coupling with nearby (not observed) $K = 1$ levels was indicated by the negative centrifugal distortion constant and the large standard deviation of the fit (0.9 MHz).³

In spite of the extremely good agreement between experimental data and theoretical values shown in Tables V–VII (in general better than 0.015 cm⁻¹), we had the problem that we could not detect a few expected subbands and could not assign the rest of the observed spectrum. Thus, a quite complete (i.e., $J = 2, \dots, 6$) Q -branch of the $K = 2$ (upper)–2 (lower) subband for the *E*-symmetry spin modification (see Fig. 6) and a Q -branch of the $K = 0(f)0(e)$ subband for the *F*-symmetry spin modification (see Fig. 7) are located well in the range of our spectrometer (110–145 GHz) but were not found in the experimental spectrum. Possibly these transitions are simply too weak to observe. Moreover, a significant number of the MMW lines reported earlier⁴ and detected in the present study were not assigned. The reason for the latter problem is that according to the calculations, the *R*- and *P*-subbands for the *E*- and *F*-levels contain only a few transitions in the searched spectral range and they have relatively high J

TABLE VII. Calculated (*ab initio*) and experimental energy levels of the CH₄-CO complex in the $j_{\text{CH}_4} = 1$ state (*F*-symmetry).

State	J	Calculation (cm ⁻¹)	Observation ^a (cm ⁻¹)	O-C (cm ⁻¹)
$K = 0(e)$	0	0.000 00	0.000 00	0.000
	1	0.190 05	0.192 16	0.002
	2	0.571 17	0.577 10	0.006
	3	1.145 06	1.156 06	0.011
	4	1.913 67	1.930 87	0.017
	5	2.878 77	2.904 01	0.025
	6	4.041 73	4.078 56	0.037

^aObtained from Ref. 4.

quantum numbers. This makes their assignment uncertain. Note that the rotational spectrum of CH₄-CO is quite complex because three internal rotor states $j_{\text{CH}_4} = 0, 1, 2$ of methane are well populated even at the low temperature in a molecular jet and multiple Coriolis interactions occur in the case of *E* ($j_{\text{CH}_4} = 2$) and *F* ($j_{\text{CH}_4} = 1$) levels.

Earlier, many other transitions, possibly corresponding to excited methane internal rotor states, were observed in the IR spectrum, but also not assigned.¹ We hope that it will be possible now to assign these transitions using combination differences from the newly observed MMW spectra of CH₄-CO and accurate *ab initio* calculations.

VI. CONCLUSIONS

This paper describes new observations of the millimeter-wave spectrum of the CH₄-CO van der Waals complex and calculation of the rovibrational bound states on a 5D intermolecular potential surface obtained through high-level *ab initio* calculations. It is evident from these studies that methane undergoes large amplitude internal rotation within the complex, resulting in the observation of rotational transitions within various internal rotor states.

The observed transitions were assigned to the $K = 2$ –1 subband correlating with the $j_{\text{CH}_4} = 0$ state (*A* symmetry) of free methane and the $K = 2$ –1 and $K = 0$ –1 subbands correlating with the $j_{\text{CH}_4} = 2$ state (*E* symmetry) of free methane. These measurements were included in a simultaneous fit together with the previous data to determine an improved set of empirical molecular parameters and energy levels scheme for both observed spin modifications. The bound rovibrational levels of all three nuclear spin species (*A*, *E*, and *F*) were computed for total angular momentum $J = 0$ –6.

It was found from the calculations that the global minimum of the 5D PES corresponds to a structure with intermolecular separation $R = 6.79 a_0$ and binding energy $D_e = 177.82 \text{ cm}^{-1}$. The CO subunit, more or less perpendicular to the axis connecting the centers of mass of the two subunits, forms a T-shaped complex and is closest to the CH₄ face. A significant fraction of the binding energy goes into the zero-point energy associated with the intermolecular vibrations and internal rotations: the dissociation energies D_0 are 91.32, 94.46, and 104.21 cm⁻¹ for the *A* ($j_{\text{CH}_4} = 0$), *F* ($j_{\text{CH}_4} = 1$), and *E* ($j_{\text{CH}_4} = 2$) nuclear spin modifications of CH₄-CO, respectively.

The computed energy levels were compared with the rotational spectra measured earlier and in the present work. We found very good agreement with experiment for all detected stacks although we noted that a significant number of the detected lines were not assigned. The reason for the latter issue may be that the spectrum is quite complex and expected subbands of the *E*- and *F*-levels contain only a few transitions with relative high J -numbers in the covered spectral range that makes their assignment not certain.

Finally, we conclude that the present results provide a considerable amount of new information, both experimental and theoretical, that elucidates the intermolecular interactions and dynamics in the CH₄-CO system.

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- ¹C. Xia, K. A. Walker, and A. R. W. McKellar, *J. Chem. Phys.* **114**, 4824 (2001).
- ²P. R. Bunker and P. Jensen, *Molecular Symmetry and Spectroscopy*, 2nd ed. (NRC Research Press, Ottawa, Canada, 1998).
- ³Y. Liu and W. Jäger, *J. Chem. Phys.* **121**, 6240 (2004).
- ⁴A. V. Potapov, A. A. Dolgov, V. A. Panfilov, L. A. Surin, and S. Schlemmer, *J. Mol. Spectrosc.* **268**, 112 (2011).
- ⁵W. Z. Alsindi, D. O. Gardner, E. F. van Dishoeck, and H. J. Fraser, *Chem. Phys. Lett.* **378**, 178 (2003).
- ⁶N. Tanaka, H. Nishikiori, and T. Fujii, Internet Electronic Conference of Molecular Design, 29 November 2003–12 December 2003, paper 5, see <http://www.biochempress.com>.
- ⁷H.-J. W. G. Knizia and T. B. Adler, *J. Chem. Phys.* **130**, 054104 (2009).
- ⁸T. H. Dunning, *J. Chem. Phys.* **90**, 1007 (1989).
- ⁹S. Albert, S. Bauerecker, V. Boudon, L. R. Brown, J.-P. Champion, M. Loëte, A. Nikitin, and M. Quack, *Chem. Phys.* **356**, 131 (2009).
- ¹⁰K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).
- ¹¹S. F. Boys and F. Bernardi, *Mol. Phys.* **19**, 553 (1970).
- ¹²F. Lique, J. Klos, and M. Hochlaf, *Phys. Chem. Chem. Phys.* **12**, 15672 (2010).
- ¹³Y. Kalugina, I. Buryak, Y. Ajili, A. Vigasin, N.-E. Jaidane, and M. Hochlaf, *J. Chem. Phys.* **140**, 234310 (2014).
- ¹⁴L. A. Surin, A. Potapov, A. A. Dolgov, I. V. Tarabukin, V. A. Panfilov, S. Schlemmer, Y. N. Kalugina, A. Faure, and A. van der Avoird, *J. Chem. Phys.* **142**, 114308 (2015).
- ¹⁵K. A. Peterson, D. E. Woon, and T. H. Dunning, Jr., *J. Chem. Phys.* **100**, 7410 (1994).
- ¹⁶H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schutz *et al.*, MOLPRO, version 2010.1, a package of *ab initio* programs, 2010, see <http://www.molpro.net>.
- ¹⁷W. Klopper, *Mol. Phys.* **99**, 481 (2001).
- ¹⁸F. Weigend, A. Kohn, and C. Hattig, *J. Chem. Phys.* **116**, 3175 (2002).
- ¹⁹C. Rist and A. Faure, *J. Math. Chem.* **50**, 588 (2011).
- ²⁰T. R. Phillips, S. Maluendes, A. D. McLean, and S. Green, *J. Chem. Phys.* **101**, 5824 (1994).
- ²¹P. Valiron, M. Wernli, A. Faure, L. Wiesenfeld, C. Rist, S. Kedžuch, and J. Noga, *J. Chem. Phys.* **129**, 134306 (2008).
- ²²T. G. A. Heijmen, T. Korona, R. Moszynski, P. E. S. Wormer, and A. van der Avoird, *J. Chem. Phys.* **107**, 902 (1997).
- ²³CFOUR, a quantum chemical program package written by J. F. Stanton, J. Gauss, M. E. Harding, P. G. Szalay with contributions from A. A. Auer, R. J. Bartlett, U. Benedikt, C. Berger, D. E. Bernholdt, Y. J. Bomble, L. Cheng, O. Christiansen, M. Heckert, O. Heun, C. Huber, T.-C. Jagau, D. Jonsson, J. Jusélius, K. Klein, W. J. Lauderdale, F. Lipparini, D. A. Matthews, T. Metzroth, L. A. Mück, D. P. O'Neill, D. R. Price, E. Prochnow, C. Puzzarini, K. Ruud, F. Schiffmann, W. Schwalbach, C. Simmons, S. Stopkowitz, A. Tajti, J. Vázquez, F. Wang, J. D. Watts and the integral packages *MOLECULE* (J. Almlöf and P. R. Taylor), *PROPS* (P. R. Taylor), *ABACUS* (T. Helgaker, H. J. Aa. Jensen, P. Jørgensen, and J. Olsen), and ECP routines by A. V. Mitin and C. van Wüllen. For the current version, see <http://www.cfour.de>.
- ²⁴J. Noga, M. Kállay, and P. Valiron, *Mol. Phys.* **104**, 2337 (2006).
- ²⁵A. van der Avoird and D. J. Nesbitt, *J. Chem. Phys.* **134**, 044314 (2011).
- ²⁶G. C. Groenenboom, P. E. S. Wormer, A. van der Avoird, E. M. Mas, R. Bukowski, and K. Szalewicz, *J. Chem. Phys.* **113**, 6702 (2000).
- ²⁷G. Tarrago, M. Dang-Nku, G. Poussigue, G. Guelachvili, and C. Amiot, *J. Mol. Spectrosc.* **57**, 246 (1975).
- ²⁸G. Guelachvili, *J. Mol. Spectrosc.* **75**, 251 (1979).
- ²⁹T. G. A. Heijmen, P. E. S. Wormer, A. van der Avoird, R. E. Miller, and R. Moszynski, *J. Chem. Phys.* **110**, 5639 (1999).
- ³⁰D. M. Brink and G. R. Satchler, *Angular Momentum*, 3rd ed. (Clarendon, Oxford, 1993).
- ³¹P. E. S. Wormer, *Mol. Phys.* **99**, 1973 (2001).
- ³²B. S. Dumesht and L. A. Surin, *Rev. Sci. Instrum.* **67**, 3458 (1996).
- ³³L. A. Surin, B. S. Dumesht, F. Lewen, D. A. Roth, V. P. Kostromin, F. S. Rusin, G. Winnewisser, and I. Pak, *Rev. Sci. Instrum.* **72**, 2535 (2001).
- ³⁴L. A. Surin, D. N. Furzikov, T. F. Giesen, S. Schlemmer, G. Winnewisser, V. A. Panfilov, B. S. Dumesht, G. W. M. Vissers, and A. van der Avoird, *J. Phys. Chem. A* **111**, 12238 (2007).