

Collision-induced rototranslational spectra of H₂-He: Accounting for the anisotropic interaction

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(Received 30 May 1985; revised manuscript received 21 February 1986)

In a previous paper [G. Birnbaum *et al.*, Phys. Rev. A **29**, 595 (1984)] the collision-induced rototranslational absorption spectra of H₂-He were computed from first principles, with the assumption of *isotropic* interaction. Here, we study the effects of the *anisotropy* on the basis of a distorted-wave approximation. Computed spectral intensities and shapes of the rotational lines differ from the previous results by less than the numerical uncertainties of the computations ($\sim 1\%$), except in the far wings where intensities are increasingly greater than comparable results based on isotropic interaction.

I. INTRODUCTION

Hydrogen (H₂) and helium are the most abundant constituents in the upper atmospheres of the outer planets. These atmospheres emit radiation in the far infrared although hydrogen and helium are both nonpolar. Trafton has pointed out^{1,2} that in the broad vicinity of the hydrogen rotational $S_0(0)$ and $S_0(1)$ lines, planetary atmospheres are opaque because of the dipoles induced in collisions of hydrogen with hydrogen or helium. While collision-induced dipoles are weak,³ typically less than 0.01 D, substantial absorption results owing to long path lengths and high densities.^{4,5} The dominating induction mechanism is the polarization of the collisional partner in the quadrupolar field of a hydrogen molecule, but lesser contributions due to higher multipole moments, electron exchange at close range, and interelectronic correlation at more distant range are also well known.³

Laboratory measurements of collision-induced absorption (CIA) spectra of several molecular systems exist.^{6,7} For discriminating comparisons of the spectroscopic measurements with the fundamental theory, and for the modeling of the absorption of planetary atmospheres,⁴ it is necessary that accurate profiles of the CIA H₂-H₂ and H₂-He rototranslational spectra are computed over a range of temperatures from about 50 to 300 K. Line-shape computations are possible if two functions of the intermolecular interaction are given, the potential and induced-dipole functions.⁸ In a previous paper,⁹ the theory of the collision-induced rototranslational absorption spectra of systems like H₂-He was formulated for anisotropic interaction, but numerical computations of such spectra are known only for the much simpler case of isotropic potentials.^{8,9} Spectra thus computed from the fundamental theory are in a reasonable, albeit less than perfect, agreement with laboratory measurements.⁹ It is not clear whether the agreement can be improved if the aniso-

tropy of the interaction is taken into account. Alternatively, the *ab initio* dipole data, the measurements, or all of these may possibly need improvements before one can rely on the fundamental theory to reproduce these important spectra correctly.

It is true that the anisotropic part of the interaction potential of the H₂-He system is relatively small and, in the end, its neglect may perhaps appear justified. However, it is also clear that for line-shape computations a small variation of the collision diameter σ of an (isotropic) potential leads to a substantially greater variation of the spectral intensities.^{8,9} More specifically, spectral intensities are proportional to the squared dipole moment, $I \sim |\mu(R)|^2$, at the separations of the spectroscopic interaction which can be roughly approximated by the collision diameter $R \simeq \sigma$. For quadrupole-induced dipoles, the dipole moment is proportional to the inverse fourth power of separation, $\mu \sim R^{-4}$, and a variation of the interaction distance of 1%, $\Delta R/\sigma \simeq 0.01$, gives thus an eight-times-greater variation of the observed intensity, $\Delta I/I \simeq -8(\Delta R/\sigma)$. For overlap-induced dipoles, on the other hand, which are exponential functions of the separation $\mu \sim \exp(-R/\rho)$, we get $\Delta I/I \simeq -(2\sigma/\rho)(\Delta R/\sigma)$, and since $2\sigma/\rho \simeq 20$ for the isotropic dipole,⁹ we see that in this case a 1% variation causes a 20% change of the spectral intensity. The point we want to make is that it is rather clear that the root of the anisotropic H₂-He potential^{10,11} varies by $\sim 3.5\%$ as the molecule is rotated through 180° relative to the intermolecular axis. Consequently, intensity variations of individual encounters may amount to $\sim 28\%$ for the quadrupole-induced rotational lines, and even more ($\sim 70\%$) for the translational component if the molecular orientations were maintained in the encounter. Albeit one would expect a considerable fraction of these variations to cancel in the average, the magnitude of these numbers amounts to a clear warning that the anisotropy of the potential may have a non-negligible effect on the spectra

We note that good spectroscopic measurements are uncertain typically by less than 10% and one would like to aim for an accuracy of the computational results which is even better (< 5%). Furthermore, the effect of the anisotropy is to mix the various induced dipole tensor components which in the isotropic-potential approximation have no interference. For example, for H₂-He the squares of the two most substantial dipole components⁹ just mentioned, isotropic overlap ($L=1, \lambda=0$) and quadrupolar induction ($L=3, \lambda=2$) determine the translational spectrum and the rotational $S_0(0), S_0(1)$ lines in the isotropic-potential approximation. These actually couple via the anisotropy of the potential so that the (1,0)-overlap component now affects the rotational line shapes, and vice versa. As far as we know, the spectroscopic effect of such coupling has never been described satisfactorily in quantitative terms. The study of the spectroscopic effects of the anisotropy of the potential appears to be indispensable.

II. THEORY

We employ a distorted-wave approximation which should model the main effects of the anisotropy reasonably closely. The theory will be described in some detail in a forthcoming paper.¹² Here, we mention that we introduce simplifying assumptions, namely, (1) that the anisotropic part of the potential is small, and (2) that the system absorbs radiation in short times, perhaps 10^{-12} sec.

Because small torques acting over long enough times may produce transitions between states of different angular momenta, a coupled set of equations has to be solved to describe the molecular scattering processes which involve relatively long times.¹³ The assumption of a small anisotropy by itself does not uncouple the equations. However, with the short-radiative-time assumption added, we may expect that during such a short time the torque is insufficient to change the angular momenta. This gives rise to a significant simplification of the numerical procedures. For example, if we estimate the torque T experienced by the hydrogen molecule during a radiative collision with a helium atom, assuming the motion is dominated by the isotropic part of the potential, we find that the integral of the torque, taken from the beginning (t_i) to the end (t_f) of the collisional interaction,

$$A = \left| \int_{t_i}^{t_f} T(t) dt \right|, \quad (1)$$

is bigger than the quantum of angular momentum (\hbar) only for high energies and low orbital angular momenta. [For example, for the Gordon-Shaefer potential,¹¹ at $T=100$ K and a kinetic energy of $E_k = k_B T/3$, A is less than \hbar regardless of the value of the angular momentum $\hbar\sqrt{l(l+1)}$. With $E_k = k_B T$, A is less than \hbar if l is greater than 2, and with $E_k = 3k_B T$, A is less than \hbar if l is equal to 5 or greater.] These considerations suggest a form of the rototranslational wave functions of the collisional system in the center-of-mass frame,

$$\psi_{j,l,JM}^E(\mathbf{R}, \hat{\mathbf{r}}) = \frac{1}{R} u_{jl}^J(\kappa R) Y_{jl}^{JM}(\hat{\mathbf{r}}, \hat{\mathbf{R}}), \quad (2)$$

where E is the total energy, j, l are the rotational and orbital angular momenta quantum numbers, J and M are the total angular momentum and its projection along a fixed direction, $\hat{\mathbf{r}}$ is the orientation of the molecule, \mathbf{R} is the vector joining the atom with the center of mass of the molecule, $\hbar^2 \kappa^2 = 2\mu[E - B_0 j(j+1)]$, m is the reduced mass, B_0 is the rotational constant of the molecule in energy units, and the Y_{jl}^{JM} are vector-coupling functions.^{9,13} If H is the rototranslational Hamiltonian, the equation for the radial wave functions $u(\kappa R)$ can be derived by imposing

$$\left[\int d\hat{\mathbf{r}} d\hat{\mathbf{R}} Y_{jl}^{JM}(H - E) Y_{jl}^{JM} \right] \frac{1}{\kappa R} u_{jl}^J(\kappa R) = 0, \quad (3)$$

from which we get

$$\left[\frac{-\hbar^2}{2\mu} \frac{d^2}{dR^2} + \frac{\hbar^2 l(l+1)}{2\mu R^2} + B_0 j(j+1) \right. \\ \left. + \langle jl; J | V | jl; J \rangle \right] u_{jl}^J(\kappa R) = E u_{jl}^J(\kappa R), \quad (4)$$

with the matrix element of the interaction potential, $\langle jl; J | V | jl; J \rangle$, as defined by Arthurs and Dalgarno.¹³ The functions u_{jl}^J are computed from Eq. (4) using numerical procedures (the same as for solving Eq. 12 of Ref. 9). The squared dipole strength $|\mu|^2$ for a transition from the state ($EJjl$) to ($E'J'j'l'$) is expressed in terms of these functions, as

$$|\mu_{E'J'j'l', EJjl}^{E'J'j'l'}|^2 = \sum_{MM'} |\langle \psi_{j'l',J'M'}^{E'} | \mu | \psi_{j'l,JM}^E \rangle|^2 \\ = (2J'+1) \left| \int_0^\infty u_{jl}^J(\kappa R) \mu^{(1)}(j'l'j'l'; R) u_{j'l',J'M'}^{E'}(\kappa' R) dR \right|^2, \quad (5)$$

with

$$\mu^{(1)}(j'l'j'l'; R) = \sum_{L\lambda} [(2j+1)(2l+1)(2J+1)(2\lambda+1)(2L+1)]^{1/2} C(IL'l'; 00) C(j\lambda j'; 00) \begin{Bmatrix} j' & l' & J' \\ j & l & J \\ \lambda & L & 1 \end{Bmatrix} A_{L\lambda}(R). \quad (6)$$

This expression contains two Clebsch-Gordan coefficients, a 9- j symbol (curly brackets), and the induced dipole tensor components $A_{L\lambda}(R)$ defined by Eq. (17) of Ref. 9. Whereas for isotropic interaction the squared dipole mo-

ment $|\mu|^2$ is given by a sum over the squares of the $A_{L\lambda}$ [see Eq. (16) of Ref. 9], we observe now interference of the various components $A_{L\lambda}$. Spectral intensities are computed by multiplying Eq. (5) by the normalized Boltzmann

factors of translational and rotational states, P_{E_i} , P_j , and summing over all states,

$$g(\omega) = \sum_{jj'} g_{jj'}(\omega) \quad (7)$$

and

$$g_{jj'}(\omega) = P_j \int_0^\infty dE_i P_{E_i} \sum_{ll'JJ'} |\mu_{E_i J J'}^{E' J' J' l'}|^2, \quad (8)$$

with $E' = \hbar\omega + E - \hbar\omega_{jj'}$, where $\omega_{jj'}$ is 2π times the rotational transition frequency of hydrogen, $j \rightarrow j'$. The spectral function $g(\omega)$ is composed of rotational and translational profiles, $g_{jj'}(\omega)$, similar as previously shown [Eq. (A6) of Ref. 9]. The rotational lines, $g_{jj'}(\omega)$ for $j < j'$, peak at the rotational frequencies $\omega_{jj'}$. The "red wings" fall off faster than the blue wings, according to the principle of detailed balance. For $j = j'$, several purely translational components are obtained ($j = 0, 1, 2, \dots$). Downward transitions ($j > j'$) may be thought of as peaking at negative frequencies; their positive-frequency parts must be included in the summation over j, j' if upper states are sufficiently populated. The absorption coefficient $\alpha(\omega)$ is related to the spectral function $g(\omega)$ as usual; see Eq. (1) of Ref. 9. We note that the Boltzmann factor P_E describing the population of the translational states contains a reciprocal volume V [see Eq. (3) of Ref. 9]. So, if both sides of Eqs. (7) and (8) are multiplied by V , the right-hand side of Eq. (8) is independent of V and can be numerically computed from known molecular properties.

III. RESULTS

For the line-shape computation of the rototranslational CIA spectra of H_2 -He, we use as before⁹ Wormer and van Dijk's *ab initio* dipole function¹⁴ and Meyer, Hariharan, and Kutzelnigg's *ab initio* interaction potential¹⁰ whose isotropic part has been used in the previous work.⁹ The sum over L, λ in Eq. (6) contains three terms, namely, the isotropic overlap ($L=1, \lambda=0$), an anisotropic overlap (1,2), and the quadrupole-induced component (3,2); higher terms are negligible.¹⁴

In Fig. 1, we compare the new results with the measurement.⁷ The various contributions are labeled with the initial and final rotational quantum numbers j, j' involved. Although we have not done this in Ref. 9, such individual profiles (j, j') can also be obtained for the case of isotropic interaction. A comparison shows that these are virtually *not discernible* from the new rotational profiles shown in the figure. Only in the far wings of the rotational profiles with $j \neq j'$, at frequency shifts of more than $\pm 300 \text{ cm}^{-1}$ from the line centers where intensities have fallen off to just a few percent or less of the peak intensity, we observe an excess intensity arising from the anisotropic interaction which amounts to $\sim 4\%$ at $\pm 300 \text{ cm}^{-1}$, that is significantly more than the numerical noise of the computations ($\sim 1\%$). Wing intensities exceed their counterparts obtained with isotropic interaction more, the greater the frequency shifts are. We believe that this fact is related to the admixture of the overlap components ($L=1, \lambda=0$ and $L=1, \lambda=2$) to the long-range quadrupolar dipole components ($L=3, \lambda=2$). It is well known that short-range overlap components are associated with much

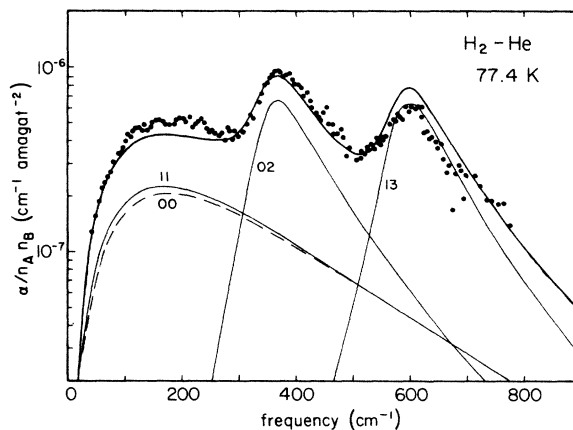


FIG. 1. Rototranslational collision-induced spectrum of hydrogen-helium pairs at 77 K. Individual lines are labeled with the initial and final rotational quantum numbers jj' involved. The heavy line gives the superposition of all lines. The dots reproduce the measurement (Ref. 7).

broader spectral profiles than, for example, the quadrupole-induced ones.

The superposition of the five components with $j, j' = 0, 0; 1, 1; 2, 2; 0, 2; \text{ and } 1, 3$ results in a spectrum (heavy line, Fig. 1) which is practically not discernible from the previous result over the frequency band shown. (We mention that for this comparison we had to correct a $\sim 15\%$ error in the $L=1, \lambda=0$ component of our previous computation⁹ that was based on the isotropic *ab initio* potential.¹⁰ This correction leads to a better consistency of line-shape computations based on the two isotropic potentials considered in Ref. 9.)

The temperature dependence of the spectral effects of the anisotropy could not be investigated in detail, but we mention that at lower temperatures, the effect of the anisotropy might be expected to be greater. A sample calculation for the temperature of 40 K indicated no significant departures from the described behavior. Only in the far wings, the effect of anisotropy was slightly greater, namely, 4.8% versus 3.7% at a shift of $+300 \text{ cm}^{-1}$ for the $jj'=02$ line at 40 and 77 K, respectively.

We note that the H_2 -He system is one of the few molecular pairs which do not form a van der Waals dimer, H_2 -He, because of the shallowness of the well. There are, therefore, no bound-state contributions to the spectra to be considered.

In conclusion, we note that we have obtained very similar results as those shown if the empirical Gordon-Shaefer potential¹¹ is substituted for the *ab initio* model.¹⁰ However, in that case, the comparison with previous results⁹ is unfortunately complicated by the fact that the isotropic part of the Gordon-Shaefer potential has been modified and does not exactly agree with Gengenbach and Hahn's model¹⁵ used previously. The small effects of the anisotropy must be studied with identical isotropic parts.

IV. CONCLUSION

We have obtained the first computations of the rototranslational CIA spectrum of H_2 -He which account for

the weak anisotropy of the interaction. The comparison with a previous calculation based on isotropic interaction potentials shows no discernible differences over the range of frequencies of the laboratory measurement. Since the anisotropy of other H_2 -rare-gas systems, and of the H_2 - H_2 system, is comparable to that of H_2 -He, one might expect similarly negligible effects for the CIA spectra of these systems near the centers of the rotational lines. The far wings of the rotational lines are, however, clearly affected by the mixing effect of the anisotropic interaction. When the wing intensities of the low-temperature roto-translational CIA spectra of H_2 -He and H_2 - H_2 are to be modeled closely at frequencies above $\sim 900\text{ cm}^{-1}$, the anisotropy of the interaction cannot be ignored.

Note added in proof Close-coupling computations of the H_2 -He roto-translational absorption spectra at 77 and

195 K have been obtained by J. Schäfer.¹⁶ From the plots we have seen of that rather rigorous work it appears that the present results are in substantial agreement. We are grateful to Dr. Schäfer for showing us his results prior to publication.

ACKNOWLEDGMENTS

Substantial amounts of class-VI computer time have been provided for this work by Cray Research, Inc., in conjunction with the University of Texas, Office of the Vice President for Research, Dr. G. J. Fonken. We thank Dr. V. Parr of Cray Research for his friendly advice and patient efforts which were invaluable. This work was supported by the National Science Foundation under Grant No. AST-83-10786.

¹L. Trafton, *Astrophys. J.* **146**, 558 (1966).

²L. Trafton, *Astrophys. J.* **147**, 765 (1967).

³W. Meyer, in *Phenomena Induced by Intermolecular Interaction*, edited by G. Birnbaum (Plenum, New York, 1985), p. 29.

⁴D. Gautier, B. Conrath, M. Flaser, R. Hanel, V. Kunde, A. Chedin, and N. Scott, *Geophys. Res.* **86**, 8713 (1981).

⁵R. H. Tipping, in *Phenomena Induced by Intermolecular Interaction*, edited by G. Birnbaum (Plenum, New York, 1985).

⁶H. L. Welsh, in *Spectroscopy*, Vol. 3 of *MTP International Review of Science*, Phys. Chem. Series One, edited by A. D. Buckingham and D. A. Ramsay (Butterworths, London, 1972).

⁷G. Birnbaum, *J. Quant. Spectrosc. Radiat. Transfer* **19**, 78 (1978).

⁸J. Borysow and L. Frommhold, in *Phenomena Induced by Intermolecular Interaction*, edited by G. Birnbaum (Plenum,

New York, 1985), p. 67.

⁹G. Birnbaum, S.-I. Chu, A. Dalgarno, L. Frommhold, and E. L. Wright, *Phys. Rev. A* **29**, 595 (1984).

¹⁰W. Meyer, P. C. Hariharan, and W. Kutzelnigg, *J. Chem. Phys.* **73**, 1880 (1980).

¹¹R. Shafer and R. Gordon, *J. Chem. Phys.* **58**, 5422 (1973).

¹²M. Moraldi, A. Borysow, J. Borysow, and L. Frommhold (unpublished).

¹³A. M. Arthurs and A. Dalgarno, *Proc. R. Soc. London, Ser. A* **256**, 540 (1960).

¹⁴P. E. S. Wormer and G. van Dijk, *J. Chem. Phys.* **70**, 5695 (1979).

¹⁵R. Gengenbach and C. Hahn, *Chem. Phys. Lett.* **15**, 604 (1972).

¹⁶J. Schäfer (private communication).