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Collision-induced absorption in He-Ar mixture*

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The absorption coefficient for collision-induced absorption in a He-Ar mixture is calculated for frequencies between 67 and 733 cm^{-1} in the 200–400 °K temperature range. Starting with a Lennard-Jones (6-12) interatomic potential derived from atomic-beam work, the absorption coefficient is computed for five different dipole-moment functions. The calculation is quantum mechanical, dynamically exact, and uses no adjustable parameters. The results are compared with the room-temperature experimental results as well as with previous theoretical work.

I. INTRODUCTION

Collision-induced absorption (CIA) in He-Ar mixtures has been the subject of a number of experimental studies. The phenomenon was first discovered by Kiss and Welsh,[1] who showed that (i) the absorption in the 350–700-cm^{-1} range was continuous and without any structure, and (ii) the absorption coefficient scaled as the product of the two gas densities. Bosomworth and Gush[2] have confirmed the He-Ar results of Kiss and Welsh and have extended the observations down to about 40 cm^{-1}. Reliable experimental results from CIA for He-Ar mixture are thus available in the 40–700-cm^{-1} region.

Theoretical work on this problem is based upon two approaches. In the statistical approach, an expression for the autocorrelation function of the dipole moment is obtained in terms of a few parameters, which are determined from the experimental data. If these parameters are similar from one pair of inert gases to another, one would say that the underlying model is reasonable. The hope in this type of calculation is that after some experience the details of the absorption process can be predicted for varied species and circumstances. The other approach is dynamical, calculating CIA from the detailed dynamics of the collision process. This method itself is applied in two ways, one with simplifications in the collision dynamics, the other from a more *a priori* standpoint. The first of these is used by Levine and Birnbaum,[3] who approximate the interatomic trajectory during the collision by a straight path. The straight path permits the atoms to come much closer than a realistic potential would. To compensate for this, these authors picked a dipole-moment function $\mu(r)=Are^{-Br^2}$, where r is the interatomic distance and A and B are adjustable parameters. This form of dipole-moment function has no physical justification, but the factor of r decreases the importance of those collisions in which the atoms have a small impact parameter. The resulting dipole-moment autocorrelation function is in surprisingly good agreement with that obtained by Sears.[4]

Also simplifying the dynamics is the work of Tanimoto.[5] He used a more realistic exponential repulsive potential, i.e., $V(r)=Ae^{-\alpha r}$, and simplified the dynamics by using the modified wave-number approximation. This approximation replaces

$$k^2 - l(l+1)/r^2$$

in the wave equation for radial motion by

$$k^2 - l(l+1)/r_{0l}^2 = k_l^2\,,$$

where r_{0l} is the classical turning point for the lth partial wave. The radial equation reduces to an s-wave equation with energy of relative motion $\hbar^2 k_l^2/2M$, and can be solved analytically for exponential repulsive potentials, $V(r)=Ae^{-\alpha r}$. Further, the integrals over the dipole-moment function can be obtained and evaluated in closed form if $\mu=A_1e^{-\alpha_1 r}$, where $\alpha_1=\alpha$ or $\frac{1}{2}\alpha$, and α is the range parameter in the interatomic potential. Tanimoto[5] obtains good agreement with the data of Kiss and Welsh in the 350–700-cm^{-1} range. However, his predictions for lower frequencies are not borne out by the experimental work of Bosomworth and Gush.

Also using the dynamical approach with simplified dynamics are Okada, Kajikawa, and Yamamoto.[6] These authors approximate the interatomic potential by a hard sphere, i.e., $V(r)=0$ for $r>d$, and $V(r)=\infty$ for $r\leq d$. Assuming a dipole-moment function $\mu(r)=A_2e^{-\alpha_2 r}$, and using classical mechanics to describe the atomic motion, they calculate CIA for Ne-Ar and He-Ar mixtures. The two adjustable parameters in the dipole-moment function are obtained from the low-frequency region of the experimental work of Bosomworth and Gush. The hope and expectation for the adjustable parameters are the same as in statistical calculations.

In the second, more *a priori*, method within the dynamical approach, the starting point is the interatomic potential and dipole-moment function, obtained from independent sources. Using classical or quantum equations of motion, the expectation value of the dipole moment, and hence the absorption coefficient, is then computed. The work of McQuarrie and Bernstein[7] on CIA in He-Ar is in this spirit. These authors used a Lennard-Jones 6-12 potential to describe the He-Ar interaction. The parameters used, $\epsilon = 3.50\times10^{-15}$ erg and $\sigma = 3.07$ Å, are derived from molecular-beam measurements of Düren, Feltgen, Gaide, Helbing, and Pauly.[8] The dipole-moment function is taken from *ab initio* calculations of Matcha and Nesbet.[9] With these input parameters, and using the classical equations of motion to calculate the trajectories, the dipole-moment function induced during the collision can be calculated and its Fourier transform obtained. The absolute square of the Fourier component at frequency ω gives, aside from constant factors, the absorption coefficient at this frequency. These authors have computed the absorption coefficient only for frequencies less than ~240 cm^{-1}, due to slow convergence of some of the integrals. The results of this study, which computes the absorption coefficient for free-free transitions, are smaller than experiment by a factor of about 3, but can be brought into agreement with experiment if the value of the range parameter ρ in the dipole-moment correlation function $\mu(r) = \mu_0 e^{-r/\rho}$ is increased by about 8% from the value calculated by Matcha and Nesbet.[9] The predictions of these authors on the temperature dependence of the absorption coefficient have not been tested experimentally. The drawback of this classical calculation is that it does not conserve energy. The energy of the system does not change after absorption of the photon.

In this paper we present a calculation of the He-Ar absorption coefficient in the McQuarrie-Bernstein spirit, but using quantum instead of classical mechanics, and imposing conservation of energy. The quantum-mechanical wave functions are used to compute the expectation value of the dipole-moment function between initial and final states. This calculation, which treats the collision dynamics exactly, should give results whose accuracy is limited only by that of the two inputs (interatomic potential and dipole-moment function), and by the numerical accuracy of the calculation. We thus believe that this approach has the advantage that, given reliable CIA experimental data and one of the two input parameters, this calculation can be used to test the proposed values of the other input parameter. For example, there have been proposed two very different dipole-moment functions due to overlapping of atomic charges for the He-Ar pair.[9,10] Although both dipole-moment calculations involve serious approximations, we believe that reliable experimental data on CIA in He-Ar mixtures might provide some evidence concerning the dependability of these approximations. There is in addition a detailed calculation of the long-range r^{-7} dipole-moment function induced by dispersion forces alone.[11] This function is 6.6 times smaller and opposite in sign to that obtained by Levine[12] for the same quantity, using a simple Drude model.

Another advantage of the present approach is that it can provide an independent check of the experimental data. For example, Kiss and Welsh[1] measured the absorption coefficient for the 1:1 He-Ne mixture to be 2.6×10^{-7} and 0.7×10^{-7} $\text{cm}^{-1}\,\text{amagat}^{-2}$ at 400 and 600 cm^{-1}, respectively. Although the failure of Bosomworth and Gush to obtain measurable absorption around 200 cm^{-1} cast some doubt on the He-Ne results of Kiss and Welsh, it was a calculation in this same spirit[13] which pointed out that the Kiss-Welsh results may be in error by about two orders of magnitude. Although the calculation is probably more laborious and certainly more expensive than the ones described earlier, we believe the reliability of the results, and the opportunity it affords to test more approximate models, justifies the additional expense.

Trafton[14] has used the approach reported here for calculating the pressure-induced spectrum in H_2. In addition, he has given expressions for CIA for atomic species. Trafton's expressions and the ones we have used are slightly different. The reason is that we take the probability of two atoms colliding with relative momenta between $\vec{k}$ and $d\vec{k}$ to be $kf(k)\,d\vec{k}$, whereas Trafton[14] takes this equal to $f(k)\,d\vec{k}$, $f(k)$ being the Boltzmann distribution function. Our additional factor of k takes account of the fact that more rapidly moving molecules collide more often.

II. ABSORPTION COEFFICIENT FOR FREE-FREE TRANSITIONS

The absorption coefficient (in $\text{cm}^{-1}\,\text{amagat}^{-2}$) at frequency ω for a transition between initial state i and final state f is given by[3,14]

$$\alpha(\omega) = \frac{4\pi^2}{c}\,\omega n_L^2 \sum_{i,f} (p_i - p_f)\,|\langle f|\vec{\mu}\cdot\hat{\epsilon}|i\rangle|^2 \times \delta(E_f - E_i - \hbar\omega), \tag{1}$$

where $n = 2.687\times10^{19}$ is the number of atoms per cm^3 at STP and $\hat{\epsilon}$ is a unit vector along the direction of polarization of the incident photon.

For the wave functions of the relative translational motion, we take

$$|i\rangle = \frac{4\pi}{kr}\sum_l i^l e^{i\delta_l} R_l(kr) \sum_m Y^*_{lm}(\hat{k}) Y_{lm}(\hat{r}), \qquad (2)$$

where r and $\hat{r}$ denote the magnitude and orientation of the distance between two nuclei, k and $\hat{k}$ denote similar quantities for the wave vector of relative motion, Y_{lm} are spherical harmonics, and $R_l(kr)$ is the solution of the differential equation

$$\frac{d^2}{dr^2} R_l(kr) + \left(k^2 - \frac{l(l+1)}{r} - \frac{2M}{\hbar^2} V(r)\right) R_l(kr) = 0, \qquad (3)$$

with boundary conditions

$$\lim_{r\to 0} R_l(kr) = 0 \qquad (3a)$$

and

$$\lim_{r\to\infty} R_l(kr) = \sin(kr - \tfrac{1}{2} l\pi + \delta_l), \qquad (3b)$$

where δ_l is the phase shift of the lth partial wave due to potential $V(r)$ at energy $\hbar^2 k^2/2M$.

In writing Eqs. (1) and (2) we have factored out the motion of the center of mass of the two atoms. We thus ignore the Doppler effect throughout the present work.

In the absence of a potential the wave function i becomes a plane wave, i.e., $\lim_{V\to 0}|i\rangle = e^{i\vec{k}\cdot\vec{r}}$. Because the potential $V(r)$ does not create or destroy particles, it conserves normalization, permitting us to calculate the incident and outgoing fluxes using plane waves.

p_i, the probability of two atoms colliding with relative momentum between $\hbar\vec{k}_i$ and $\hbar(\vec{k}_i + d\vec{k}_i)$, is given by

$$p_i = \frac{(2\pi)^{-3} k_i^3\, dk_i\, d\Omega(\hat{k}_i) \exp[-(\hbar^2 k_i^2/2M)\beta]}{[4\pi/(2\pi)^{-3}] \int_0^\infty k^3\, dk \exp[-(\hbar^2 k^2/2M)\beta]}$$
$$= \frac{1}{2\pi}\left(\frac{\beta\hbar^2}{2M}\right)^2 k_i^3 \exp\left(-\beta\frac{\hbar^2 k_i^2}{2M}\right) dk_i\, d\vec{\Omega}(\hat{k}_i), \qquad (4)$$

where $\beta = 1/k_B T$, k_B is the Boltzmann constant, and T is the temperature in degrees kelvin. The factor $(2\pi)^{-3}$ comes from the fact that for unit volume, the number of states in the interval $\vec{k}$ and $\vec{k} + d\vec{k}$ is $k^2\, dk\, d\Omega/(2\pi)^3$. The sum over the final states is written as

$$(2\pi)^{-3} \int_0^\infty k_f^2\, dk_f \int d\vec{\Omega}_f . \qquad (5)$$

Equations (4) and (5) differ by a factor k because the probability that two atoms collide is taken to be $kf(\vec{k})$, where $f(\vec{k})$ is the distribution function. From Eqs. (7)–(11) we get

$$\alpha(\omega) = \frac{16\pi^2}{3c}\, \omega n_L^2 \beta^2 \hbar (2M)^{-1/2} \int_0^\infty dE\, (E + \hbar\omega)^{-1/2} e^{-\beta E}\left[1 - \left(1 + \frac{\hbar\omega}{E}\right)^{1/2} e^{\beta\hbar\omega}\right] I(k_i, k_f), \qquad (6)$$

where

$$I(k_i, k_f) = \sum_l [l I_{l,l-1} + (l+1) I_{l,l+1}] \qquad (7)$$

is the sum over partial waves and

$$I_{l,l_1} = \left(\int_0^\infty R_l(k_i r) R_{l_1}(k_f r)\, \mu(r)\, dr\right)^2, \qquad (8)$$

where $\mu(r)$ is the dipole-moment function and k_f is determined by the energy conservation relation

$$k_f = (k_i^2 + 2M\omega/\hbar)^{1/2}.$$

III. BOUND-TO-FREE TRANSITIONS

In this type of transition the two atoms form a molecule in the initial state. This molecule may be a true bound state with negative energy, or it may be a positive energy state trapped in the centrifugal barrier (resonant state). In either case, an absorption process corresponds to photodissociation of the molecule. Because the He-Ar potential has a well depth of only about 17.5 cm^{-1}, He-Ar has only one bound vibrational state, which supports five rotational states. Their energies, calculated using Lennard-Jones (6-12) potential,

$$V(r) = \epsilon[(r_m/r)^{12} - 2(r_m/r)^6],$$

with $\epsilon = 0.350\times 10^{-14}$ erg and $r_m = 3.45$ Å, are −5.756, −5.178, −4.039, −2.377, and −0.272 cm^{-1}.

Because of the small binding energy these states are scarcely populated at room temperature. We will, therefore, ignore their contribution to CIA.

IV. COMPUTATIONS

The dipole transition probabilities to be evaluated are of the form

$$\sum_{l=0}^{N} [l I_{l,l-1} + (l+1) I_{l,l+1}]. \qquad (9)$$

Typical values of N required for convergence of the sum to three figures are 50. The integrals are

$$I_{l,l'} = \left(\int_0^\infty R_l(k_i r) R_{l'}(k_f r) \mu(r)\, dr\right)^2, \qquad (10)$$

where $\mu(r)$ is the collision-induced dipole moment and $R_l(k_i r)$ and $R_{l'}(k_f r)$ are the radial wave functions of the initial and final states, of angular momentum quantum numbers l and l'. The five forms of $\mu(r)$ for which we calculated CIA are defined in Table I.

The integrals are calculated in straightforward fashion, first obtaining the wave functions and then evaluating the integrals by Simpson's rule.

The wave functions are stored on tape for reuse. The wave functions are calculated for each l using the double-precision program DPHCG from the IBM Scientific Subroutine Package. This solves differential equations numerically using a Milne-Hamming predictor-corrector method. This is a stable fourth-order "stepping" method (i.e., using given initial values, as distinct from boundary conditions), with good error control.

The differential equations to be solved are the standard radial part of the Schrödinger equation [Eq.(9)], with the given interatomic potential. The solution must be known at some point to provide initial values. This point is taken far enough inside the classically forbidden region that the wave function is essentially zero, and the equation integrated outward from there. This yields a solution to within normalization, with the normalization factor easily found after the solution has attained the asymptotic limit,

$$R_l(kr) \xrightarrow[k\to\infty]{} \sin(kr - \tfrac{1}{2}l\pi + \delta_l), \tag{11}$$

where δ_l is the phase shift of the lth partial wave. For a minimum in the He-Ar interatomic potential at 3.45×10^{-8} cm, typically 750 points of the wave function are stored, out to a distance of 50×10^{-8} cm. Error control, to attain the desired three-figure accuracy in the final sum over integrals, was done experimentally, by adjusting the wave function tolerance which is input to the program DHPCG; by altering the intervals at which the wave functions are stored, for input to the Simpson's rule integration; and by observing how high l must be carried in the final sum. Typical IBM 370-165 CPU times for calculating 50 wave functions for $l=0\rightarrow50$, for a single initial or final state (i.e., a single energy), are 5 min, with 10 min thus required for an entire sum over integrals. This approach is simple and direct, with maximum use of stock "library" programs; but probably at the expense of greater efficiency attainable from programs tailored for these calculations.

The five bound-state energies were obtained using essentially the same programs as were used to calculate the wave functions. The simple scheme was merely to iteratively adjust the energies (now negative instead of positive) in the radial part of the Schrödinger equation [Eq. (16)], until the wave function yielded by the calculation obeyed as well as possible the condition

$$\lim_{r\to\infty} R_l(kr) = 0,$$

in addition to being zero at the origin. The Schrödinger equation was the negative-energy analog of Eq. (3), with $k^2 \rightarrow -k^2$.

TABLE I. Values of collision-induced absorption (10^{-7} cm^{-1} amagat^{-2}) for He-Ar mixture at room temperature. The theoretical induced dipole moments are [in atomic units: r in a_0's, $\mu(r)$ in ea_0, a_0 is Bohr radius, and e is electronic charge; He$^+$Ar$^-$ taken as positive] (i) L-BB. Lacey and Byers-Brown overlap term (read from Fig. 1 of Ref. 10): $\mu_{\text{L-BB}}(r)=31.6e^{-1.530r}$; (ii) M-N. Matcha and Nesbet overlap term (Fig. 1 of Ref. 9): $\mu_{\text{M-N}}(r)=13.3e^{-1.472r}$; (iii) W-BB. Whisnant and Byers-Brown dispersion term (Table XI of Ref. 11): $\mu_{\text{W-BB}}(r)=-125/r^7$. (Note that this has opposite polarity to the first two.)

	Experimental		Theoretical					
			Present calculations					
Transition frequency (cm^{-1})	Kiss and Welsh [Fig. 1(a) of Ref. 1]	Bosomworth and Gush (Fig. 2 of Ref. 5)	L-BB + W-BB	M-N + W-BB	L-BB overlap only	M-N overlap only	W-BB dispersion only	Classical M-N calculations (Fig. 2 of Ref. 7, $\rho^*=0.117$)
67	···	3.0	2.6	0.70	3.4	1.1	0.047	1.1
133	···	6.8	6.2	1.6	7.8	2.5	0.086	2.2
200	···	7.5	7.1	1.9	8.8	2.7	0.087	2.2
267	···	5.8	6.4	1.6	7.8	2.4	0.073	1.6 (extrapolated)
333	5.2 (extrapolated)	3.7	5.0	1.2	6.2	1.8	0.056	···
400	2.6	2.2	3.7	0.88	4.5	1.3	0.041	···
467	1.2	1.2	2.6	0.61	3.2	0.91	0.029	···
533	0.63	0.63 (extrapolated)	1.8	0.42	2.2	0.63	0.021	···
600	0.35	0.31 (extrapolated)	1.2	0.29	1.5	0.43	0.015	···
667	0.15	···	0.86	0.19	1.1	0.29	0.011	···
733	···	···	0.60	0.13	0.74	0.20	0.0075	···

TABLE II. Calculated values of collision-induced absorption (10^{-7} cm^{-1} $amagat^{-2}$) for He-Ar mixture as a function of temperature, calculated from the theoretical induced dipole moment, $\mu(r) = \mu_{\text{L-BB}}(r) + \mu_{\text{W-BB}}(r)$, as defined in Table I.

Temperature (°K)	Transition frequency (cm^{-1}) 67	133	200	267	333	400	467	533	600	677	733
200	3.1	6.1	5.9	4.6	3.2	2.1	1.4	0.89	0.56	0.37	0.24
250	2.8	6.2	6.6	5.6	4.2	2.9	2.0	1.3	0.88	0.59	0.40
300	2.6	6.2	7.1	6.4	5.0	3.7	2.6	1.8	1.2	0.86	0.60
350	2.4	6.1	7.5	7.1	5.8	4.4	3.2	2.3	1.6	1.2	0.82
400	2.3	6.0	7.7	7.6	6.5	5.1	3.9	2.9	2.1	1.5	1.1

V. RESULTS AND DISCUSSION

Ideally, the dipole-moment function for He-Ar should be calculated in a manner which takes electron correlation into account, such as a Hartree-Fock calculation including configuration interaction. Such a calculation is presently unavailable. There are three approximate calculations of dipole-moment function available in the literature.

On the one hand, there is the molecular Hartree-Fock calculation of Matcha and Nesbet (M-N),[9] which is probably a better picture of the real situation at small internuclear distances. On the other hand is the calculation of Lacey and Byers-Brown[10] (L-BB), which approximates the overlap contribution to the dipole moment by electron exchange between undistorted Hartree-Fock atoms. Because these calculations involve different assumptions, it is not unreasonable to assume that each one may be a better representation of the physical situation in a restricted interval.

Neither of these calculations includes the contribution of the dispersion forces to the dipole-moment function. The leading dispersion term in the dipole-moment function has been computed by Whisnant and Byers-Brown[11] (W-BB). In this work we will calculate CIA due to these three dipole-moments functions, as well as the two dipole-moment functions obtained by adding the W-BB dispersion contribution to the M-N and L-BB overlap contributions.

This simple addition of overlap and dispersion parts has scant theoretical justification. However, this customary procedure is the best currently available. It yields the correct dipole-moment function at large internuclear distances where the dispersion term dominates, and, at the smallest internuclear distances realized in the collisions presently under consideration, where the overlap term dominates, reduces to the desired M-N or L-BB overlap form.

Several potential functions for He-Ar have been proposed. Matcha and Nesbet,[9] from their molecular Hartree-Fock calculation discussed earlier, proposed an exponential repulsive potential for the inert-gas atoms. Colgate *et al.*[15] and Kemnev and Leonas[16] have investigated the He-Ar potential for energies in the 1-eV range, i.e., about 8000 cm^{-1}. However, since we will deal with relative energies in the 200–1200-cm^{-1} range, these results are not useful to us. Walker and Westenberg[17] have interpreted their diffusion work (300–1000°K) assuming only a repulsive part for the He-Ar potential.

In the present study we will use the potential arrived at from the molecular-beam work of Düren *et al.*[8] Not only is this investigation in the energy interval of direct interest to us (200–3000 m/sec relative velocity), but also the results were interpreted using both an attractive and a repulsive part, which is more realistic than a solely repulsive potential. In addition, this potential was also

TABLE III. Calculated values of collision-induced absorption ($10^{-7}$$cm^{-1}$ $amagat^{-2}$) for He-Ar mixture as a function of temperature, calculated from the M-N overlap term plus the W-BB dispersion term: $\mu(r) = \mu_{\text{M-N}}(r) + \mu_{\text{W-BB}}(r)$, as defined in Table I.

Temperature (°K)	Transition frequency (cm^{-1}) 67	133	200	267	333	400	467	533	600	667	733
200	0.83	1.6	1.5	1.2	0.78	0.50	0.32	0.20	0.13	0.082	0.054
250	0.76	1.6	1.7	1.4	1.0	0.69	0.46	0.31	0.20	0.13	0.088
300	0.70	1.6	1.9	1.6	1.2	0.88	0.61	0.42	0.29	0.19	0.13
350	0.65	1.6	1.9	1.8	1.4	1.1	0.77	0.54	0.38	0.26	0.18
400	0.60	1.6	2.0	1.9	1.6	1.2	0.91	0.66	0.47	0.33	0.24

TABLE IV. Calculated values of collision-induced absorption (10^{-7} cm^{-1} amagat^{-2}) for He-Ar mixture as a function of temperature, calculated from the L-BB overlap induced dipole only: $\mu_{\text{L-BB}}(r)$, as defined in Table I.

Temperature	Transition frequency (cm^{-1})										
(°K)	67	133	200	267	333	400	467	533	600	667	733
200	3.9	7.5	7.3	5.6	3.9	2.6	1.7	1.1	0.70	0.45	0.30
250	3.6	7.8	8.2	6.8	5.1	3.5	2.4	1.6	1.1	0.73	0.49
300	3.4	7.8	8.8	7.8	6.2	4.5	3.2	2.2	1.5	1.1	0.74
350	3.1	7.7	9.3	8.7	7.1	5.4	4.0	2.9	2.0	1.4	1.0
400	2.9	7.5	9.5	9.3	7.9	6.3	4.7	3.5	2.6	1.8	1.3

used in the earlier He-Ar CIA work of McQuarrie and Bernstein,[7] and thus facilitates comparison with their results.

Finally, in our earlier study on CIA in He-Ne, we directly tested the effect of the potential adopted. The He-Ne potential of Düren *et al.* was mainly used, but a limited amount of this work was duplicated using the M-N He-Ne potential, with essentially the same results. We believe that in the range of internuclear distances of interest, this is probably again the case.

Table I gives the results of our calculations at 300°K using the five different dipole-moment functions mentioned, and compares them with the experimental work of Kiss and Welsh, and with that of Bosomworth and Gush. We also show the theoretical results of McQuarrie and Bernstein (McQ-B). This calculation uses the same interatomic potential and dipole-moment function as our "M-N overlap only" column, and differs from the latter only in using classical instead of quantum mechanics. It is gratifying to note that our results agree with those of McQ-B where one might expect the latter to be most valid, namely, at 67 cm^{-1}. The McQ-B calculation does not conserve energy; i.e., the absorbed photon does not affect the translational motion of the atoms—an approximation which should be least serious at small photon energies, and most serious at large, where, indeed, our energy-conserving results differ from McQ-B. In particular, our calculations show that most of the contribution to the absorption coefficient at frequencies below 240 cm^{-1} (where McQ-B obtained their results), comes from atoms colliding with a relative energy of 300–500 cm^{-1}. While it may be reasonable to take translational kinetic energy as conserved if a 67-cm^{-1} photon is absorbed, this seems less plausible for a 240-cm^{-1} photon.

In the early discussion[12] of the validity of the M-N induced dipole-moment function, there figured largely the latter's neglect of the r^{-7} dispersion term. It is interesting that for He-Ar this term is relatively unimportant. Its inclusion or neglect affects the calculated results substantially less than the choice of overlap part: whether L-BB overlap or M-N overlap. Levine,[12] using a simple Drude model, early obtained the result that the r^{-7} dispersion term in the induced dipole moment by itself accounts for 60–90% of the experimental He-Ar zeroth moment for absorption. By contrast, our corresponding results for the absorption coefficient are nearer 1%. These results given in the "W-BB dispersion only" column of Table I were obtained using the induced dipole moment resulting from the much more sophisticated calculation of BB-W.

Table I shows that for low absorption frequencies, including the bulk of the room-temperature absorption, the L-BB + W-BB induced dipole moment function gives results closer to experiment than does the M-N + W-BB function, while for high frequencies this situation is reversed. Our experience is that the transition-moment integral

TABLE V. Calculated values of collision-induced absorption (10^{-7} cm^{-1} amagat^{-2}) for He-Ar mixture as a function of temperature, calculated from the M-N overlap induced dipole only: $\mu_{\text{M-N}}(r)$, as defined in Table I.

Temperature	Transition frequency (cm^{-1})										
(°K)	67	133	200	267	333	400	467	533	600	667	733
200	1.3	2.4	2.3	1.7	1.2	0.74	0.48	0.31	0.19	0.13	0.082
250	1.2	2.5	2.5	2.1	1.5	1.0	0.69	0.46	0.30	0.20	0.14
300	1.1	2.5	2.7	2.4	1.8	1.3	0.91	0.63	0.43	0.29	0.20
350	1.0	2.4	2.9	2.6	2.1	1.6	1.1	0.81	0.57	0.40	0.28
400	0.95	2.4	2.9	2.8	2.4	1.8	1.4	0.99	0.71	0.51	0.36

TABLE VI. Calculated values of collision-induced absorption (10^{-7} cm^{-1} amagat^{-2}) for He-Ar mixture as a function of temperature, calculated from the W-BB dispersion induced dipole only: $\mu_{\text{W-BB}}(r)$, as defined in Table I.

Temperature (°K)	Transition frequency (cm^{-1}) 67	133	200	267	333	400	467	533	600	667	733
200	0.055	0.081	0.070	0.051	0.035	0.023	0.015	0.010	0.0067	0.0045	0.0031
250	0.051	0.085	0.080	0.063	0.046	0.032	0.022	0.015	0.011	0.0072	0.0051
300	0.047	0.086	0.087	0.073	0.056	0.041	0.029	0.021	0.015	0.011	0.075
350	0.043	0.086	0.092	0.081	0.065	0.050	0.037	0.027	0.020	0.014	0.010
400	0.040	0.084	0.096	0.088	0.073	0.058	0.044	0.033	0.025	0.018	0.013

is largely determined by the magnitude of the induced dipole moment at the classical turning point—presumably because the radial wave functions are least rapidly oscillating there. Table I thus implies that the M-N induced dipole moment function is more accurate at internuclear distances equal to the classical turning points associated with high frequencies. These imply high translational energies, and thus generally smaller classical turning points. This is in accord with the expectation that the M-N calculation is most accurate at small distances, and that the L-BB calculation, based on electron exchange between undistorted Hartree-Fock atoms, is more accurate at larger distances. We estimate the distance at which one dipole-moment function becomes more accurate than the other as about 2.4–2.5 Å: The two functions yield about equally accurate results for the 400-cm^{-1} transitions, and the main contributions to this transition come from wave functions corresponding to classical turning points in this range.

In Tables II–VI, we give the temperature dependence of absorption coefficient as a function of frequency for the five dipole-moment functions, for future comparison with experiment, as well as with more approximate models.

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