

Effect of the vibrational dependence of intermolecular potential on the spectral line shifts for the case of diatomic molecules

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Equations have been derived that allow for the dependence of intermolecular potential on the level of vibrational excitation of an absorbing molecule in calculations of the spectral line shifts. The intermolecular potential in the form of a sum of atom-atom Lennard–Jones intermolecular potentials is used. Equations for calculation of matrix elements of the intermolecular potential with the allowance made for the vibrational dependence are obtained for diatomic and triatomic molecules. The contribution coming from the vibrational addition of the intermolecular potential to the Ar-pressure induced shift of HF spectral lines is assessed.

Introduction

Characteristics of the intermolecular interaction potential are of interest when calculating relaxation parameters of a spectral line profile: halfwidth, line shifts, and cross-relaxation parameters, as well as in studying intermolecular interactions. Various forms of the intermolecular potential (IMP) are used in calculations of spectral line shifts. In Refs. 1–3, long-range electrostatic dipole-dipole, dipole-quadrupole, quadrupole-quadrupole, and other interactions are considered. Labany et al. in Ref. 4 use the summed IMP: long-range electrostatic part and short-range potential represented by a sum of coupled atom-atom Lennard–Jones potentials. In our earlier papers,^{5–7} we took the summed IMP in the following form: long-range electrostatic part and polarization (induction and dispersion) interactions. In Refs. 8 and 9, the IMP is taken as a sum of long-range electrostatic, short-range atom-atom, and polarization parts. At the same time, no one paper considered the dependence of IMP characteristics on the degree of vibrational excitation of a molecule and the constants of various forms of the IMP were thought independent of vibrational quantum numbers.

Earlier it was shown^{5–7} that polarization interactions make the major contribution to line shifts in the near-IR and visible regions. For example, in Refs. 5–7 the contribution to shifts of H₂O, NO₂, and SO₂ spectral lines induced by N₂, O₂, and noble gas pressure makes up 75–85% for lines due to transitions to highly excited states. Therefore, the problem of the account for the vibrational dependence of IMP characteristics is still urgent. In Ref. 10, we have developed the method for taking into account the dependence of constants of the Lennard–Jones potential on the degree of vibrational excitation of an absorbing molecule. This work is devoted to further development of the approach proposed in Ref. 10.

Intermolecular potential within the framework of Robert–Bonamy theory

In Ref. 4, Labany et al. have developed an approach to description of the IMP by taking it as a sum of long-range electrostatic and short-range parts. The short-range part of the IMP was represented as a sum of atom-atom Lennard–Jones potentials for every pair of colliding molecules. Analytical equations were derived for halfwidth and line shift within the framework of the spectral broadening theory.² The IMP V^{tot} for a system of colliding molecules was represented as a sum of electrostatic and atom-atom parts:

$$V^{\text{tot}} = V^{\text{elec}} + V^{\text{at-at}}. \quad (1)$$

The short-range part of the IMP $V^{\text{at-at}}$ was expressed as a sum of Lennard–Jones potentials for every pair of colliding atoms. In the case of collision of a diatomic molecule with an atom, the short-range part of the IMP was written as

$$V^{\text{at-at}} = 4 \sum_{i=1}^2 \epsilon_i \left\{ \frac{(\sigma_i)^{12}}{(r_i)^{12}} - \frac{(\sigma_i)^6}{(r_i)^6} \right\}, \quad (2)$$

where ϵ_i and σ_i are characteristics of the Lennard–Jones potential to the i th pair of atoms; r_i is the intermolecular separation (separation between the centers of gravity of the i th atom of the absorbing molecule and the disturbing atom).

It should be noted that Eq. (2) is the general form of the IMP, because it includes both the repulsive part (the term in braces proportional to $1/r^{12}$), and the attractive one (the term in braces proportional to $1/r^6$). Then the isotropic part of the IMP was separated out through averaging over orientations of the colliding particles. As a result, the isotropic part of the IMP was represented as a series over inverse powers of the separation R between the centers of gravity of the colliding particles:

$$V_{\text{iso}} = \frac{B_6}{R^6} + 5 \frac{B_8}{R^8} + 14 \frac{B_{10}}{R^{10}} + \frac{B_{12}}{R^{12}} + 22 \frac{B_{14}}{R^{14}} + \frac{1001}{5} \frac{B_{16}}{R^{16}} + \dots \quad (3)$$

Here B_{2n} are constants including the equilibrium separations between the centers of gravity and the parameters ϵ_i and σ_i of the Lennard–Jones potential. The anisotropic part of the short-range potential $V^{\text{at-at}}$ was ignored in Ref. 4. To calculate the matrix elements of V_{iso} and then halfwidths, the constants B were fitted to the experimental values of the Lennard–Jones potential. The obtained effective values of the constants B were used for calculation of halfwidths. It should be noted that the approach developed in Ref. 4 ignores oscillations of atoms of the absorbing molecule about the equilibrium position, the dependence of the separation R on the degree of vibrational excitation, and the vibrational dependence of the IMP.

In Refs. 8 and 9, the obtained IMP in the form (3) along with the polarization terms was used for calculation of the shifts of H_2O spectral lines induced by the pressure of O_2 , N_2 , noble gases, and CO_2 . It should be noted that Eq. (3) already contains the polarization (induction and dispersion) interactions, which, according to Ref. 11, can be written as an infinite perturbation series over inverse powers of the separation R :

$$V_{\text{iso}}(R) = V_{\text{ind}} + V_{\text{disp}}; \quad V_{\text{iso}}(R) = \sum_{n=6}^{\infty} \frac{C_n}{R^n} \quad (4)$$

In Eq. (4), C_n are constants depending on the molecular constants of colliding molecules: polarizability, dipole moment, ionization potentials. Comparison of Eqs. (3) and (4) shows that they are identical. Thus, the terms corresponding to polarization interactions were taken into account for the second time in Refs. 8 and 9. This leads to errors about 20% when comparing the measured shifts of H_2O spectral lines with those calculated with the potential from Refs. 8 and 9. Neglect of the vibrational dependence of the IMP in calculating line shifts also leads to marked errors, which may increase strongly at further vibrational excitation of the absorbing molecule.

General consideration of the intermolecular interaction potential

Consider the expansion of the potential $V^{\text{at-at}}$ (2) into a Taylor series over normal coordinates q :

$$V^{\text{at-at}}(R, q) = V_0(R) + \sum_i V_i(R) q_i + \sum_{ij} V_{ij}(R) q_i q_j + \dots \quad (5)$$

Here V_0 is the IMP at the equilibrium point; V_i are first derivatives of the IMP with respect to the

intermolecular separation R ; V_{ij} are the second derivatives of the IMP with respect to R . The line shift is determined by the difference between the matrix elements of $V^{\text{at-at}}$ in the vibrational states i (initial) and f (final) of the absorbing molecule. For quasi-rigid triatomic molecules of the C_{2v} symmetry group, like H_2O , the difference between the matrix elements of the IMP can be presented as

$$\begin{aligned} \langle \Psi_i | V^{\text{at-at}} | \Psi_i \rangle - \langle \Psi_f | V^{\text{at-at}} | \Psi_f \rangle = & \sum_n V_{nn} (V_n^i - V_n^f) - \\ & - \left[\frac{3k_{111}}{\omega_1} V_1 + \frac{k_{112}}{\omega_2} V_2 \right] (V_1^i - V_1^f) - \\ & - \left[\frac{3k_{222}}{\omega_2} V_2 + \frac{k_{122}}{\omega_1} V_1 \right] (V_2^i - V_2^f) - \\ & - \left[\frac{k_{113}}{\omega_3} V_1 + \frac{k_{233}}{\omega_2} V_2 \right] (V_3^i - V_3^f). \end{aligned} \quad (6)$$

Here $n = 1, 2, 3$ is the number of a vibration; ω_n are the harmonic frequencies; k are the anharmonicity constants; V_1 and V_2 are the first and second derivatives of $V^{\text{at-at}}$ with respect to R . Let us restrict our consideration to the second term in the series (5) and (6). For diatomic molecules of the $C_{\infty v}$ symmetry group, like HF, the difference between the matrix elements of $V^{\text{at-at}}$ is written as

$$\begin{aligned} \langle \Psi_i | V^{\text{at-at}} | \Psi_i \rangle - \langle \Psi_f | V^{\text{at-at}} | \Psi_f \rangle = \\ = \left[V_2(R) - \frac{3k_3}{\omega} V_1(R) \right] (V^i - V^f). \end{aligned} \quad (7)$$

Let us consider only the isotropic part of $V^{\text{at-at}}$, since the isotropic part of IMP makes the dominant contribution to the line shift in the near-IR and visible regions.⁵⁻⁷ To analyze numerically the vibrational dependence of $V^{\text{at-at}}$ and determine the contribution to the line shift, we should find the first and second derivatives with respect to R . Consider a system of colliding particles that consists of the absorbing HF molecule and the disturbing Ar atom (Fig. 1). Rewrite $V^{\text{at-at}}$ (2) for the specific system shown in Fig. 1 as

$$\begin{aligned} V^{\text{at-at}} = 4\epsilon_{\text{FAr}} \left\{ \frac{\sigma_{\text{FAr}}^{12}}{r_{\text{FAr}}^{12}} - \frac{\sigma_{\text{FAr}}^6}{r_{\text{FAr}}^6} \right\} + \\ + 4\epsilon_{\text{HAr}} \left\{ \frac{\sigma_{\text{HAr}}^{12}}{r_{\text{HAr}}^{12}} - \frac{\sigma_{\text{HAr}}^6}{r_{\text{HAr}}^6} \right\}. \end{aligned} \quad (8)$$

The first term here determines the interaction between the F and Ar atoms, and the second one is for the interaction between the H and Ar atoms. In Eq. (8) the following designations are introduced:

$$\epsilon_{\text{FAr}} = (\epsilon_{\text{F}} + \epsilon_{\text{Ar}})/2; \quad \epsilon_{\text{HAr}} = \sqrt{\epsilon_{\text{F}} \epsilon_{\text{Ar}}}.$$

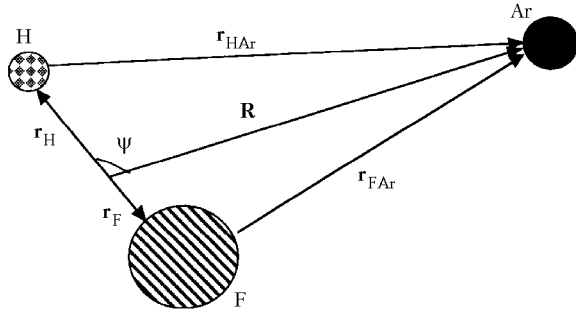


Fig. 1. System of colliding particles HF and Ar: \mathbf{R} is radius vector of separation between the centers of gravity of the colliding particles; \mathbf{r}_H and \mathbf{r}_F are radius-vectors of separations from the center of gravity of HF molecule to H and F atoms; \mathbf{r}_{HAr} and \mathbf{r}_{FAr} are radius-vectors of separations from H and F atoms to Ar atom; Ψ is the angle between the axis of HF molecule and the direction toward Ar atom.

In a polar coordinate system, the separations and the angle in Fig. 1 can be written in terms of the radius-vector and the azimuth angle:

$$\mathbf{R} - \mathbf{r}_F = \mathbf{r}_{FAr}, \quad \mathbf{R} - \mathbf{r}_H = \mathbf{r}_{HAr}; \quad \Psi = \Psi(\theta, \varphi). \quad (9)$$

According to the cosine theorem, the separations between the atoms can be written as

$$r_{FAr} = \sqrt{R^2 + r_F^2 - 2Rr_F \cos \Psi}, \quad (10)$$

$$r_{HAr} = \sqrt{R^2 + r_H^2 - 2Rr_H \cos \Psi}.$$

The separations between the atoms of the absorbing molecule and the disturbing atom in Fig. 1 depend on the amplitude of atomic vibrations in the absorbing molecule. Let us determine the separation between the Ar atom and the H and F atoms using the equilibrium distance r^e and the vibrational addition Δr . The higher is the vibrational excitation of the HF molecule, the larger the deviations Δr from the equilibrium separation r^e :

$$r = r^e + \Delta r, \quad r_F = r_F^e + \Delta r_F, \quad r_H = r_H^e + \Delta r_H. \quad (11)$$

Expand the potential (8) into Taylor series over the vibrational separations Δr_F and Δr_H using Eqs. (10) and (11). The coefficients of the Taylor series are the derivatives of $V^{\text{at-at}}$ with respect to Δr_F and Δr_H at $\Delta r_F = 0$ and $\Delta r_H = 0$. Restricting our consideration to the second term of the series, we obtain the following equation for the coefficients of the series:

$$V_0|_{\Delta r_F=0} = 4\epsilon_{FAr} \left\{ \frac{\sigma_{FAr}^{12}}{\left[\sqrt{R^2 + (r_F^e)^2 - 2Rr_F^e \cos \Psi} \right]^{12}} - \frac{\sigma_{FAr}^6}{\left[\sqrt{R^2 + (r_F^e)^2 - 2Rr_F^e \cos \Psi} \right]^6} \right\} + 4\epsilon_{HAr} \{F \rightarrow H\};$$

$$\left. \frac{\partial V}{\partial r_F} \right|_{\Delta r_F=0} = 4\epsilon_{FAr} \left\{ \frac{12\sigma^{12}(r_F^e - R \cos \Psi)}{\left[\sqrt{R^2 + (r_F^e)^2 - 2Rr_F^e \cos \Psi} \right]^{14}} - \frac{6\sigma^6(r_F^e - R \cos \Psi)}{\left[\sqrt{R^2 + (r_F^e)^2 - 2Rr_F^e \cos \Psi} \right]^8} \right\} + 4\epsilon_{HAr} \{F \rightarrow H\}; \quad (12)$$

$$\left. \frac{\partial^2 V}{\partial (r_F)^2} \right|_{\Delta r_F=0} = 4\epsilon_{FAr} \left\{ \frac{168\sigma^{12}(r_F^e - R \cos \Psi)^2}{\left[\sqrt{R^2 + (r_F^e)^2 - 2Rr_F^e \cos \Psi} \right]^{16}} + \frac{12\sigma^{12}}{\left[\sqrt{R^2 + (r_F^e)^2 - 2Rr_F^e \cos \Psi} \right]^{14}} \right\} - \left\{ \frac{48\sigma^6(r_F^e - R \cos \Psi)^2}{\left[\sqrt{R^2 + (r_F^e)^2 - 2Rr_F^e \cos \Psi} \right]^{10}} + \frac{6\sigma^6}{\left[\sqrt{R^2 + (r_F^e)^2 - 2Rr_F^e \cos \Psi} \right]^8} \right\} + 4\epsilon_{HAr} \{F \rightarrow H\}.$$

The Taylor series for the atom-atom Lennard-Jones potential with the coefficients (12) has the following form:

$$V^{\text{at-at}} = V_{0F}|_{\Delta r_F=0} + \left. \frac{\partial V}{\partial (\Delta r_F)} \right|_{\Delta r_F=0} \cdot (\Delta r_F) + \left. \frac{\partial^2 V}{\partial (\Delta r_F)^2} \right|_{\Delta r_F=0} \cdot (\Delta r_F)^2 + V_{0H}|_{\Delta r_H=0} + \left. \frac{\partial V}{\partial (\Delta r_H)} \right|_{\Delta r_H=0} \cdot (\Delta r_H) + \left. \frac{\partial^2 V}{\partial (\Delta r_H)^2} \right|_{\Delta r_H=0} \cdot (\Delta r_H)^2. \quad (13)$$

This equation determines the dependence of the potential (8) for the system of colliding particles HF-Ar on the vibrational separations Δr_F and Δr_H in the HF molecule. It is seen from Eq. (13) that $V^{\text{at-at}}$ nonlinearly depends on the vibrational additions Δr_F and Δr_H . Since the line shift is determined largely by the matrix elements of the isotropic part of $V^{\text{at-at}}$ (Refs. 5-7), it may increase strongly as the separations Δr_F and Δr_H increase at vibrational excitation of the HF molecule.

Determine the addition to the HF-Ar line shift due to the vibrational dependence of $V^{\text{at-at}}$ at the vibrational excitation of HF molecules. First let us find the isotropic part of $V^{\text{at-at}}$ by expanding Eq. (13) into Taylor series over $\cos \Psi$ and restricting the consideration to the first term $\cos \Psi = 0$. Thus we obtain the

following equations for the coefficients independent of $\cos\Psi$:

$$\begin{aligned}
 V_0|_{\cos\Psi=0} &= 4\varepsilon_{\text{FAr}} \left\{ \frac{\sigma_{\text{FAr}}^{12}}{\left[\sqrt{R^2 + (r_{\text{F}}^e)^2}\right]^{12}} - \right. \\
 &\quad \left. - \frac{\sigma_{\text{FAr}}^6}{\left[\sqrt{R^2 + (r_{\text{F}}^e)^2}\right]^6} \right\} + 4\varepsilon_{\text{HAr}} \{F \rightarrow H\}, \\
 V_1|_{\cos\Psi=0} &= 4\varepsilon_{\text{FAr}} \left\{ \frac{12\sigma_{\text{FAr}}^{12} r_{\text{F}}^e}{\left[\sqrt{R^2 + (r_{\text{F}}^e)^2}\right]^{14}} - \right. \\
 &\quad \left. - \frac{6\sigma_{\text{FAr}}^6 r_{\text{F}}^e}{\left[\sqrt{R^2 + (r_{\text{F}}^e)^2}\right]^8} \right\} \cdot (\Delta r_{\text{F}}) + 4\varepsilon_{\text{HAr}} \{F \rightarrow H\} \cdot (\Delta r_{\text{F}}),
 \end{aligned} \quad (14)$$

$$\begin{aligned}
 V_2|_{\cos\Psi=0} &= 4\varepsilon_{\text{FAr}} \left\{ \frac{168\sigma_{\text{FAr}}^{12} (r_{\text{F}}^e)^2}{\left[\sqrt{R^2 + (r_{\text{F}}^e)^2}\right]^{16}} - \right. \\
 &\quad \left. - \frac{12\sigma_{\text{FAr}}^{12} (r_{\text{F}}^e)}{\left[\sqrt{R^2 + (r_{\text{F}}^e)^2}\right]^{14}} \right\} \cdot (\Delta r_{\text{F}}) - 4\varepsilon_{\text{HAr}} \times \\
 &\quad \times \left\{ \frac{48\sigma_{\text{FAr}}^6 (r_{\text{F}}^e)^2}{\left[\sqrt{R^2 + (r_{\text{F}}^e)^2}\right]^{10}} - \frac{6\sigma_{\text{FAr}}^6 (r_{\text{F}}^e)^2}{\left[\sqrt{R^2 + (r_{\text{F}}^e)^2}\right]^8} \right\} \times \\
 &\quad \times (\Delta r_{\text{F}})^2 + 4\varepsilon_{\text{HAr}} \{F \rightarrow H\} \cdot (\Delta r_{\text{H}})^2.
 \end{aligned}$$

To find the line shift, we should know molecular characteristics. Let us write the equations for the masses of the H and F atoms and the separations from the atoms to the center of gravity of the HF molecule:

$$\begin{cases} m_{\text{H}} \Delta r_{\text{H}} - m_{\text{F}} \Delta r_{\text{F}} = 0, \\ \Delta r_{\text{H}} + \Delta r_{\text{F}} = \Delta r. \end{cases} \quad (15)$$

Find the separations Δr_{F} and Δr_{H} :

$$\Delta r_{\text{F}} = \frac{m_{\text{H}} \Delta r}{m_{\text{H}} + m_{\text{F}}}, \quad \Delta r_{\text{H}} = \Delta r \left(1 - \frac{m_{\text{H}}}{m_{\text{H}} + m_{\text{F}}} \right). \quad (16)$$

Using the equation from Refs. 2 and 7 for calculation of the interruption function in the first order of the perturbation theory

$$\begin{aligned}
 S_1 &= \frac{1}{\hbar} \int_{-\infty}^{+\infty} dt [\langle v_f | V^{\text{at-at}}(R) | v_f \rangle - \\
 &\quad - \langle v_i | V^{\text{at-at}}(R) | v_i \rangle] \quad (17)
 \end{aligned}$$

and calculating the matrix elements of the atom-atom potential in the form (13) with the coefficients (14) accounting for the vibrational additions, we obtain the equation for the contribution of the function S_1 to the line shift:

$$S_1 = \frac{A}{b^{n-1}} \int_0^{\infty} \frac{dz}{(\sqrt{1+z^2})^n}. \quad (18)$$

Here b is the impact parameter; A is some constant containing the matrix elements of the isotropic part of the IMP, molecular characteristics of the absorbing molecule HF and the disturbing atom Ar; the integration variable is $z = (v/b)t$, where t is time. According to Ref. 12, the integrals of the type (18) can be expressed analytically as:

$$\int_0^{\infty} \frac{dz}{(z^2 + 1)^n} = \frac{\pi}{2} \frac{(2n-3)!!}{2^{n-1} (n-1)!}. \quad (19)$$

Thus, calculation of the contribution of the function S_1 to the line shift is reduced to algebraic calculations. Using the matrix elements of $V^{\text{at-at}}$ (7) with the allowance made for the vibrational dependence, we can calculate the contribution to the HF-Ar spectral line shift. For this purpose, we used the molecular constants for the band 0-2, $n=8$. It turned out that the allowance for the vibrational dependence of $V^{\text{at-at}}$ contributes about 11% to the line shift as compared to calculation neglecting the vibrational dependence. For the lines due to the transitions to higher excited vibrational states, the contribution to the shift coming from the vibrational addition of the IMP must increase. The obtained result indicates that the vibrational dependence of the isotropic part of the IMP should be taken into account in calculating spectral line shifts.

Conclusion

Thus, the equations enabling one to allow for the dependence of the IMP on the degree of vibrational excitation of the absorbing molecule have been derived. The matrix elements of the isotropic part of the IMP in the form of atom-atom Lennard-Jones potentials are calculated for triatomic and diatomic molecules. The general equation (18) and (19) is obtained for the contribution of the isotropic part of the IMP to the spectral line shift; the obtained equation is convenient for numerical calculations. The contribution to the HF-Ar line shift from the vibrational addition to the IMP in the form of the Lennard-Jones potential has been estimated. This contribution makes up to 11%.

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