Vibrational Structure and Predissociation of Ar-CO_2 by CO_2 Symmetric Stretching Mode Coupled with Ar Motion

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The computationally simple quantum mechanical method (VSCF-DWB-IOS) has been applied to studying the Ar-CO_2 vibrational predissociation phenomenon. The new methodology utilizes the vibrational self-consistent field method to determine the vibrational structure of the van der Waals complex, the distorted-wave Born approximation for dissociating process, and the infinite-order sudden approximation for the continuum dissociating product of CO_2. The dissociation due to the coupling of the symmetric stretching vibrational motion of CO_2 with the motion of the Ar van der Waals mode has been extensively investigated. The lifetimes of transient excited vibrational states, linewidths of absorption peak, and the rotational state distributions of the product, CO_2 have been computed. It has been found that the lifetime of the Ar-CO_2 in excited vibrational state is very long compared with that of triatomic van der Waals complexes and the product CO_2 carries a major portion of dissociation energy as a rotational energy.

Keywords : Vibrational structure, Predissociation, Ar-CO_2.

Introduction

The study, both experimentally and theoretically, on intramolecular energy transfer within a van der Waals complex has become an interesting research subject. The vibrational predissociation is one of important phenomena caused by intramolecular energy transfer. For large van der Waals complexes the identification and distributions of vibrational predissociation products have been a major subject to investigate, while very detailed dynamics of vibrational predissociation has been pursued for small complexes. Particularly the vibrational predissociation of triatomic (atom-diatom) van der Waals complexes has been extensively studied.[1] The detailed predissociation dynamics of large complexes (larger than triatomics) have not been studied much because of the complexity of the systems. Therefore it is still challenging to determine the full (including highly excited states) vibrational structure of large van der Waals complexes as well as their dynamics.

One of the tetra-atomic systems that has received a lot of experimental and theoretical attention is the Ar-CO_2 complex. Many theoretical investigations have focused on the potential energy surface (PES) of the ground electronic state of the Ar-CO_2 complex because its vibrational dynamics is very sensitive to the details of the PES.[2-12] With those theoretical PES, the equilibrium structure and properties of Ar-CO_2 have been investigated but the full dynamics and/or composite vibrational structures were not studied yet. And the previous PES studies concentrated on the van der Waals interaction of Ar with CO_2 ignoring the dependency of potential energy on vibrational motion of CO_2, *i.e.*, CO_2 is assumed to be rigid. Experimental studies on infrared spectra, Raman pressure broadening, scattering phenomena, transport properties, and nuclear spin relaxation of Ar-CO_2 have also been reported.[13-29] All these studies were for understanding mainly either the interaction of Ar with CO_2 or the nature of the van der Waals bond. The vibrational predissociation of Ar-CO_2 has been rarely studied. Long time ago Miller's group reported two works on the vibrational predissociation but they reported only vibrational and rotational propensity rules, *e.g.*, the distribution of the CO_2 product, and thus studied the structure of the complex for the sole purpose of deducing a reasonable PES.[26,27]

Here we present a quantum mechanical study on the vibrational predissociation of Ar-CO_2. The infrared irradiation excites the vibrational motion of Ar-CO_2, mainly the incident photon energy flows into the vibrational motion of CO_2. Then the excited state relaxes into a lower level to dissociate the van der Waals bond by releasing the relaxation energy. It is the V → T (vibrational to translational) energy transfer and called the vibrational predissociation process. The dissociation occurs *via* the coupling of CO_2 vibrational motion with the van der Waals motion of Ar. To study this vibrational predissociation we should accurately determine the vibrational structure of the system, *i.e.*, wave functions and energies of excited vibrational states must be calculated. Ar-CO_2 has 6 vibrational degrees of freedom so that accurate quantum mechanical calculations of excited vibrational states are still a formidable task.[30] Moreover in this dynamics work we have to evaluate the continuum wave functions of dissociating products, which is too complicated to handle when all the 6 degrees of freedom are included. To reduce the dimensionality of the system we decide to concentrate on the vibrational predissociation by the symmetric stretching motion of CO_2 only. The two bending motions and the

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antisymmetric stretching motions of CO_2 are ignored so that our Ar-CO_2 has only 3 vibrational degrees of freedom. CO_2, as a matter of fact, is a very rigid molecule so that the couplings among CO_2 vibrational modes are very small. Therefore our approach in which the symmetric stretching motion is free from other vibrational modes does not impose any serious errors. Only limitation of this approach is that we do not study the predissociation caused by the antisymmetric stretching or bending motions of CO_2. Of course, the stretching and bending motions of Ar atom against CO_2 are fully accounted.

The details of the theoretical method called VSCF-DWB-IOS have been reported already.[31-33] In this method the predissociation is viewed as a half-collision process. We start with determining the excited vibrational states of Ar-CO_2. The excited state of Ar-CO_2 is obtained by infrared irradiation and this absorption process is very fast compared to dissociation process. Therefore we start our calculation to determine the vibrational wave functions of the bound Ar-CO_2 in excited state. To have the wave functions we employ the vibrational self-consistent field approximation (VSCF) of which validity is verified.[34] The continuum wave function of the dissociating Ar + CO_2 should also be evaluated and the infinite-order sudden (IOS) approximation is adopted for this purpose. Then the dissociation rate is evaluated using distorted-wave Born (DWB) approximation that is essentially identical with the well known Fermi's golden rule. This VSCF-DWB-IOS method is relatively new so that the test of the methodology itself is one of the purposes of this work. The quantities we calculated are the predissociation rates, the lifetimes of the transient excited vibrational states of Ar-CO_2, the linewidths of absorption peaks, and the rotational state distributions of the dissociation product CO_2.

Theory

CO_2 has four vibrational modes - a symmetric stretching, an antisymmetric stretching, and two bending modes. In this work we concentrate only on the symmetric stretching mode (excluding the other three modes). Then the Ar-CO_2 has 3 vibrational degrees of freedom. They are the symmetric stretching motion of CO_2, the stretching and bending motions of Ar with respect to CO_2. Consequently the triatomic CO_2 can be treated as a pseudo diatomic molecule and the Ar-CO_2 (atom-triatom system) becomes an atom-diatom system. We have already developed the VSCF-DWB-IOS method for atom-diatom system and thus it can be applied to the current Ar-CO_2 predissociation study without any change.[31-33]

When CO_2 vibrates in symmetric stretching mode, the center carbon atom is stationary and the two oxygen atoms move inward and outward in a symmetric fashion. Mathematically it is identical with the vibrational motion of diatomic O_2 molecule. The only difference is the potential energy function. Therefore, from now on, we simulate the symmetric stretching vibration of CO_2 with a vibration of pseudo-O_2. Using the Jacobi coordinates system, the distance vector between the two oxygen atoms is denoted $\boldsymbol{r}$, the vector from the carbon atom to the argon atom is denoted $\boldsymbol{R}$, and the angle between $\boldsymbol{R}$ and $\boldsymbol{r}$ is θ.

The reduced Schrödinger equation for the vibrational motion is

$$H(r, R,\theta)\ \Psi(r, R,\theta) = E\Psi(r, R,\theta) \tag{1}$$

where the reduced Hamiltonian can be written as

$$H(r, R, \theta) = -\frac{1}{2\mu_1}\frac{\partial^2}{\partial r^2} - \frac{1}{2\mu_2}\frac{\partial^2}{\partial R^2} + \frac{\mathbf{j}^2}{2\mu_1 r^2} + \frac{\mathbf{l}^2}{2\mu_2 R^2} + V_1(r) + V_2(r, R, \theta) \tag{2}$$

where μ_1 is the reduced mass of two oxygen atoms, and μ_2 is the reduced mass of CO_2 and Ar atom. $\mathbf{j}$ and $\mathbf{l}$ are the two angular momenta associated with $\boldsymbol{r}$ and $\boldsymbol{R}$, respectively. When $\mathbf{J} = \mathbf{j} + \mathbf{l} = 0$,

$$\mathbf{j}^2 = \mathbf{l}^2 = \frac{-1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right). \tag{3}$$

The total potential energy of the system can be divided as $V(r, R,\theta) = V_1(r) + V_2(r, R,\theta)$ where $V_1(r)$ is the potential energy function responsible for the symmetric stretching of CO_2 (or the potential function of pseudo-O_2) and $V_2(r, R,\theta)$ is the rest of the total potential function.

The Eq. (1) is solved for a bound vibrational state by using self-consistent field (VSCF) approximation and for a dissociating continuum state by using the infinite-order sudden (IOS) approximation. When the bound state solution is designated as $\Psi^i_{\upsilon_1\upsilon_2\upsilon_3}(r, R, \theta)$ and the dissociating state solution as $\Psi^f_{\upsilon' j}(r, R, \theta)$, the dissociation rate R is under the distorted-wave Born

$$R(\upsilon_1\upsilon_2\upsilon_3 \rightarrow \upsilon' j) = \frac{2\pi}{\hbar}\rho(E)\left|\langle\, \Psi^f_{\upsilon' j}(r, R, \theta)\middle|V_c\middle|\,\Psi^i_{\upsilon_1\upsilon_2\upsilon_3}(r, R, \theta)\rangle\right|^2 \tag{4}$$

(DWB) approximation. υ_i is the vibrational quantum number of Ar-CO_2 (see below). υ' is the quantum number associated with free CO_2 symmetric stretching vibration, and j is the quantum number associated with free CO_2 molecular rotation. The V_c and $\rho(E)$ will be defined later.

The outline of VSCF procedure is as follows. We assume that the bound state wave function can be approximated as

$$\Psi^i_{\upsilon_1\upsilon_2\upsilon_3}(r, R, \theta) \approx \Psi^{\mathrm{SCF}}_{\upsilon_1\upsilon_2\upsilon_3}(r, R, \theta) = \psi^1_{\upsilon_1}(r)\,\psi^2_{\upsilon_2}(R)\,\psi^3_{\upsilon_3}(\theta) \tag{5}$$

and

$$H^{\mathrm{SCF}}(r, R, \theta)\,\Psi^{\mathrm{SCF}}_{\upsilon_1\upsilon_2\upsilon_3}(r, R, \theta) = E^{\mathrm{SCF}}_{\upsilon_1\upsilon_2\upsilon_3}\,\Psi^{\mathrm{SCF}}_{\upsilon_1\upsilon_2\upsilon_3}(r, R, \theta) \tag{6}$$

The quantum number υ_1 corresponds to the symmetric stretching motion of CO_2, υ_2 is the quantum number for the stretching motion of Ar with respect to CO_2, and υ_3 is the bending motion of Ar with respect to CO_2.

Then the modal wave functions ψ should satisfy

$$H^{\mathrm{SCF}}(r, R, \theta) = h_1(r) + h_2(R) + h_3(\theta) \tag{7}$$

$$h_1(r)\,\psi^1_{\upsilon_1}(r) = \varepsilon^1_{\upsilon_1}\,\psi^1_{\upsilon_1}(r) \tag{8}$$

$$h_2(R)\,\psi^2_{\upsilon_2}(R) = \varepsilon^2_{\upsilon_2}\,\psi^2_{\upsilon_2}(R) \tag{9}$$

$$h_3(\theta)\,\psi^3_{\upsilon_3}(\theta) \;=\; \varepsilon^3_{\upsilon_3}\,\psi^3_{\upsilon_3}(\theta) \qquad (10)$$

where, $\varepsilon^1_{\upsilon_1}$, $\varepsilon^2_{\upsilon_2}$, and $\varepsilon^3_{\upsilon_3}$ are modal eigenvalues, and

$$h_1(r) \;=\; \frac{1}{2\mu_1}\frac{\partial^2}{\partial r^2} + \frac{1}{2\mu_1 r^2}\langle \mathbf{j}^2\rangle_\theta + V_1(r) + \langle V_2(r, R, \theta)\rangle_{R,\,\theta} \qquad (11)$$

$$h_2(R) \;=\; -\frac{1}{2\mu_2}\frac{\partial^2}{\partial R^2} + \frac{1}{2\mu_2 R^2}\langle \mathbf{l}^2\rangle_\theta + \langle V_2(r, R, \theta)\rangle_{r,\,\theta} \qquad (12)$$

$$h_3(\theta) \;=\; \left\langle\frac{1}{2\mu_1 r^2}\right\rangle_r \mathbf{j}^2 + \left\langle\frac{1}{2\mu_2 R^2}\right\rangle_R \mathbf{l}^2 + \langle V_2(r, R, \theta)\rangle_{r,\,R}\;. \qquad (13)$$

The subscripts after bracket < > indicate that the quantity is an integral over the modal functions which the subscript designates. The total VSCF energy for the (υ_1, υ_2, υ_3) bound state is

$$E^i_{\upsilon_1\upsilon_2\upsilon_3} \approx E^{\mathrm{SCF}}_{\upsilon_1\upsilon_2\upsilon_3} = \varepsilon^1_{\upsilon_1} + \varepsilon^2_{\upsilon_2} + \varepsilon^3_{\upsilon_3} + E_{cor} \qquad (14)$$

where the correction energy E_{cor} is

$$E_{cor} \;=\; -\left\langle\frac{1}{2\mu_1 r^2}\right\rangle_r \langle\mathbf{j}^2\rangle_\theta - \left\langle\frac{1}{2\mu_2 R^2}\right\rangle_R \langle\mathbf{l}^2\rangle_\theta - 2\langle V_2(r, R, \theta)\rangle_{r,R,\theta} \qquad (15)$$

We turn to determination of a final state wave function, $\Psi^f_{\upsilon' j}(r, R, \theta)$ where υ' and j indicate the symmetric stretching vibrational and the rotational quantum number of free CO_2, respectively. Here we use a vibrationally adiabatic approximation, which is

$$\Psi^f_{\upsilon' j}(r, R, \theta) \approx \psi^d_{\upsilon'}(r)\,\psi^E_j(R, \theta) \qquad (16)$$

where $\psi^d_{\upsilon'}(r)$ is the symmetric stretching vibrational wave function of the state υ' of CO_2, which is a solution of the vibrational Schrödinger equation of CO_2 (or pseudo-O_2).

$$\left[-\frac{1}{2\mu_1}\frac{\partial^2}{\partial r^2} + V_1(r)\right]\psi^d_{\upsilon'}(r) \;=\; E^d_{\upsilon'}\,\psi^d_{\upsilon'}(r) \qquad (17)$$

where $E^d_{\upsilon'}$ is the υ' symmetric stretching vibrational energy of free CO_2.

The continuum wave function $\psi^E_j(R, \theta)$ consists of two parts; one is the rotational (j) motion of CO_2 and the other is a relative translational motion of CO_2 with respect to Ar. The Schrödinger equation for $\psi^E_j(R, \theta)$ is

$$\left[-\frac{1}{2\mu_2}\frac{\partial^2}{\partial R^2} + \frac{1}{2\mu_2 R^2}\mathbf{l}^2 + \left\langle \psi^d_{\upsilon'}(r)\left|\frac{1}{2\mu_1 r^2}\right|\psi^d_{\upsilon'}(r)\right\rangle \mathbf{j}^2\right.$$
$$\left. + \langle \psi^d_{\upsilon'}(r)|V_2(r, R, \theta)|\psi^d_{\upsilon'}(r)\rangle - (E^i_{\upsilon_1\upsilon_2\upsilon_3} - E^d_{\upsilon'})\right]\psi^E_j(R, \theta)=0 \qquad (18)$$

Under IOS, we set $\mathbf{j}^2 = \bar{j}(\bar{j}+1) = \mathbf{l}^2$ because total angular momentum is fixed as zero, then the scattering equation we obtain is one-dimensional, *i.e.*,

$$\left[-\frac{1}{2\mu_2}\frac{\partial^2}{\partial R^2} + \frac{1}{2\mu_2 R^2}\bar{j}(\bar{j}+1) + B\bar{j}(\bar{j}+1)\right.$$
$$\left. + \overline{V}_2(R;\theta) - E\right]\psi^E_{\bar{j}}(R;\theta) = 0 \qquad (19)$$

where B is a rotational constant of CO_2 at the symmetric stretching vibrational state υ' [the third term in Eq. (18)], $\overline{V}_2(R;\theta)$ is the averaged V_2 integral over $\psi^d_{\upsilon'}(r)$ [the fourth term in Eq. (18)], E is the translational energy which is $E^i_{\upsilon_1\upsilon_2\upsilon_3} - E^d_{\upsilon'}$, and $\psi^E_{\bar{j}}(R;\theta)$ parametrically depends on angle θ.

The dissociation process is assumed to be due to mode-mode coupling which causes energy transfer (and predissociation) from vibrational motion of Ar-CO_2 to kinetic motion of Ar (V → T). The coupling, V_c is generally so weak that a perturbative approach could be suitable (see Eq. 4) and, consequently, V_c could be regarded as

$$\begin{aligned} V_c \;&=\; H - H^{\mathrm{SCF}} \\ &=\; \frac{1}{2\mu_1 r^2}\mathbf{j}^2 - \left\langle\frac{1}{2\mu_1 r^2}\right\rangle_r \mathbf{j}^2 - \frac{1}{2\mu_1 r^2}\langle\mathbf{j}^2\rangle_\theta + \frac{1}{2\mu_2 R^2}\mathbf{l}^2 \\ &\quad - \left\langle\frac{1}{2\mu_2 R^2}\right\rangle_R \mathbf{l}^2 - \frac{1}{2\mu_2 R^2}\langle \mathbf{l}^2\rangle_\theta + V_2(r, R, \theta) \\ &\quad - \langle V_2(r, R, \theta)\rangle_{R,\,\theta} - \langle V_2(r, R, \theta)\rangle_{r,\,\theta} \\ &\quad - \langle V_2(r, R, \theta)\rangle_{r,\,R} - E_{cor} \end{aligned} \qquad (20)$$

The density of final state at energy E, $\rho(E)$, is unity when the energy-normalized continuum wave function is used.

The predissociation rate R from the (υ_1, υ_2, υ_3) initial Ar-CO_2 state to the (υ_1', j) final CO_2 state can be evaluated using Eq. (4). The full width at half-maximum (FWHM), Γ is

$$\Gamma(\upsilon_1\upsilon_2\upsilon_3 \to \upsilon' j) \;=\; \hbar R(\upsilon_1\upsilon_2\upsilon_3 \to \upsilon' j) \qquad (21)$$

$$\Gamma(\upsilon_1\upsilon_2\upsilon_3) = \sum_{\upsilon'}\sum_{j}(\upsilon_1\upsilon_2\upsilon_3 \to \upsilon' j) \qquad (22)$$

And a predissociation lifetime of the (υ_1, υ_2, υ_3) state, τ is

$$\tau(\upsilon_1\upsilon_2\upsilon_3) \;=\; \frac{\hbar}{\Gamma(\upsilon_1\upsilon_2\upsilon_3)}\;. \qquad (23)$$

Potential Energy Surface and Computations

Various types of *ab initio* and semiempirical calculations on the potential energy function of Ar-CO_2 have appeared in literatures and also many fitted potential functions using experimental data have been reported.[2-12] However all these studies concentrated on the van der Waals interaction potential between CO_2 and Ar. The CO_2 in Ar-CO_2 was always assumed to be a rigid rod in equilibrium linear geometry. In this work, since we are interested in the stretching vibrational motion of CO_2, the potential energy surface which should depend on the C-O internuclear distance is required. Therefore we constructed a new potential energy function for Ar-CO_2 using the already published potential energy functions as follows.

The total potential energy function for Ar-CO_2 is approximated as the sum of several interactions. That is,

$$V(r, R, \theta) = V_{CO_2}(r) + V_{Ar-C}(R) + 2V_{Ar-O}(r, R, \theta). \quad (24)$$

Here the r coordinate represents the CO_2 symmetric stretching vibration, R is the distance from the C in CO_2 to Ar atom, and θ is the angle between the R and r. For details of the coordinates, please refer to the Theory section. The zero of the potential energy is set to be the complete dissociation limit of Ar + C + O + O.

In spectroscopic experiment the vibrational energy of CO_2 is expressed in a virial form,[35]

$$\begin{aligned} G(v_1, v_2, v_3) = {} & \omega_1(v_1+1/2) + \omega_2(v_2+1/2) + \omega_3(v_3+1/2) \\ & + x_{11}(v_1+1/2)^2 + x_{22}(v_2+1/2)^2 + x_{33}(v_3+1/2)^2 \\ & + x_{12}(v_1+1/2)(v_2+1/2) + x_{23}(v_2+1/2)(v_3+1/2) \\ & + x_{13}(v_1+1/2)(v_3+1/2) + \cdots \end{aligned} \quad (25)$$

where v_1, v_2, and v_3 are the symmetric stretching, the bending, and the antisymmetric stretching vibrational quantum numbers of CO_2, respectively. If we ignore the bending and antisymmetric stretching motions and also the interactions among the modes, we have the energy expressions only for the symmetric stretching vibration of CO_2 in a second virial form,

$$G(v_1) \approx \omega_1(v_1+1/2) + x_{11}(v_1+1/2)^2 \quad (26)$$

where $\omega_1 = 1354.07$ cm^{-1} and $x_{11} = -3.10$ cm^{-1}. As well known, this form of vibrational energy expression can be readily obtained when a potential function between two atoms in diatomc molecule is a Morse type function.[36] Therefore the symmetric stretching potential of CO_2 is assumed to be a Morse type function, *i.e.*,

$$V_{CO_2}(r) = D_1\{1 - \exp[-\beta_1(r - r_{1e})]\}^2 - D_1 . \quad (27)$$

The r is the distance between the two end oxygen atoms because the center carbon atom is stationary in the symmetric stretching vibration. As mentioned before, the CO_2 is viewed as a pseudo-O_2 molecule. With the experimental values (ω_1 and x_{11}), the dissociation energy D_1 is calculated to be 0.673715 au (=147863 cm^{-1}) and the exponential factor β_1 to be 0.6418 au^{-1}. Marshall *et al.*[6] reported that the C-O equilibrium bond length of CO_2 is 2.194 au so that the equilibrium internuclear distance (r_{1e}) between the two oxygen atoms in pseudo-O_2 is 4.388 au.

From the Marshall *et al.*'s Ar-CO_2 potential[6] and the Cybulski *et al.*'s Ar-O_2 potential functions,[37] we constructed the Morse type potential energy function for the Ar-C interaction energy. The difference between the interaction energy of Ar-CO_2 and that of Ar-O_2 is assumed to be equal to the interaction energy between Ar and C. And the parameters are adjusted to reproduce the energy difference accurately. The resulting Ar-C potential function is

$$V_{Ar-C}(R) = D_2\{1 - \exp[-\beta_2(R - R_{2e})]\}^2 - D_2 \quad (28)$$

where $D_2 = 4.061 \times 10^{-4}$ au, $\beta_2 = 0.8169$ au^{-1}, and $R_{2e} = 6.58$ au.

The potential function for the Ar-O pair is also approximated as a Morse type function, *i.e.*,

$$\begin{aligned} & 2V_{Ar-O}(r, R, \theta) \\ & = D_3\{1 - \exp[-\beta_3(\sqrt{r^2/4 + R^2 - rR\cos\theta} - r_{3e})]\}^2 - D_3 \\ & + D_3\{1 - \exp[-\beta_3(\sqrt{r^2/4 + R^2 + rR\cos\theta} - r_{3e})]\}^2 - D_3 . \end{aligned} \quad (29)$$

The parameters are generated to fit the Cybulski *et al.*'s Ar-O_2 potential function accurately.[37] The best fitted parameters are: $D_3 = 2.649 \times 10^{-4}$ au, $\beta_3 = 0.8431$ au^{-1}, and $r_{3e} = 6.936$ au.

The greatest error in our newly suggested potential function may stem from using the sum of several Morse type functions. To reduce this error we have performed a fitting to obtain the Morse parameters. The new potential function at $r = r_{1e}$ is plotted in Figure 1. We have reproduced the correct T-shape equilibrium geometry and our fitted potential function is found to be exactly identical with the *ab initio* potential[6] within the range of $R = 6.15$-7.31 au and theta $\theta = 72$-108°. It suggests that at least the low vibrational levels of Ar-CO_2 can be accurately determined using our new potential. Note that our potential function explicitly includes and expresses the interaction energy between the CO_2 stretching and Ar atom.

We first concentrate on determining the vibrational structure of the Ar-CO_2 complex with our new potential energy surface. The vibrational state of Ar-CO_2 is denoted as (υ_1, υ_2, υ_3) where υ_1 is related with r representing the symmetric stretching motion of CO_2, and υ_2 (or R) and υ_3 (or θ) represent the stretching and bending vibrational motion of the Ar atom with respect to the CO_2. The vibrational states are calculated using the suggested VSCF method where relevant equations are numerically and iteratively solved.

For the r and R coordinates, the starting point of numerical integration is well inside the classically forbidden region. The integration ends at very large distance where the bound state wave function converges to zero and the continuum wave function becomes a plane wave, free from the interaction. For the angle(θ) coordinate, the discrete variable representation is adopted and the 81 Legendre functions, that is, 81 grid points are used. The masses of C, O, and Ar atoms are 12, 16, and 40 amu, respectively.

Within the electronic ground state of Ar-CO_2, the vibrational predissociation can be written as Ar-CO_2 (υ_1, υ_2, υ_3) → $CO_2(\upsilon')$ + Ar where υ' is less than υ_1 usually. The equa-tions presented in the previous Theory section are nume-rically solved one-by-one in order to obtain the dissociating wave functions (IOS used by setting $\bar{j} = j$), the couplings, and then the predissociation widths of absorption peaks and rotational state distributions of the

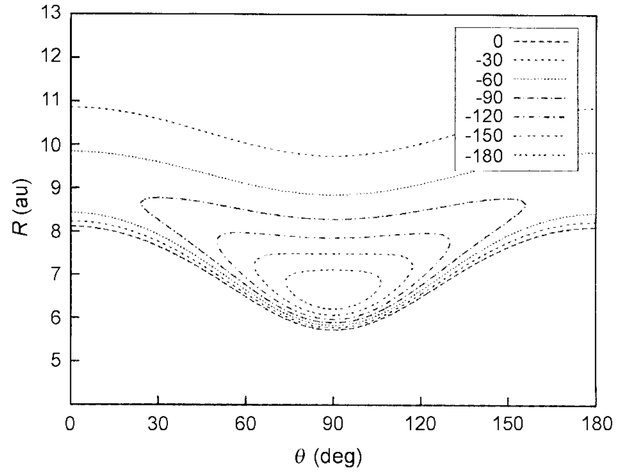

Figure 1. The contour plot of the potential energy surface (cm^{-1}) when $r = r_{1e} = 4.388$ au.

product CO_2. Same calculations are repeated for various (υ_1, υ_2, υ_3) levels and various υ' CO_2 symmetric stretching levels, that is, many dissociation channels are investigated.

Results and Discussions

To assess the accuracy of the potential energy function used, we have calculated the symmetric stretching vibrational levels of CO_2 which are listed in Table 1. Overall our theoretical values are in very good agreement with experimental ones and the agreement is better for the low vibrational levels. The calculated levels with our new Morse type potential function are generally lower than the corresponding experimental ones. The errors stem from mainly the neglect of coupling between the antisymmetric stretching and/or bending motion with the symmetric stretching motion. But the errors are generally very small (less than 0.002%) so that such discrepancy does not impose any serious problems in our dynamics calculations. We study the predissociations involving only the lower levels of CO_2.

The vibrational energy levels of Ar-CO_2 which are calculated using the vibrational self-consistent field approximation are listed in Table 2. The levels are, in this work, denoted as (υ_1, υ_2, υ_3) where υ_1 indicates the symmetric stretching of CO_2, υ_2 represents the stretching of Ar with respect to CO_2, and υ_3 is for the bending motion of Ar with respect to CO_2. υ_2 and υ_3 describe the so called van der Waals vibrational modes. For each value of υ_1, there are four υ_2 stretching states found and for each of υ_1 and υ_2, four υ_3 bending states are found. For example, when $\upsilon_1 = 0$, there are 16 bound states found; they are (0,0,0), (0,0,1), (0,0,2), (0,0,3), (0,1,0), (0,1,1), (0,1,2), (0,1,3), (0,2,0), (0,2,1), (0,2,2), (0,2,3), (0,3,0), (0,3,1), (0,3,2), and (0,3,3). Usually the bending states lie lower than the stretching states, *e.g.*, the (0,0,1) state lies lower than the (0,1,0) state. In Table 2 only some of these levels, *i.e.*, (υ_1,0,0), (υ_1,1,0), and (υ_1,0,1), are listed.

The ground vibrational state (0,0,0) of Ar-CO_2 has the vibrational energy of -172.07 cm^{-1} with respect to the ground $\upsilon' = 0$ state of CO_2. This value is cited as the dissociation energy D_o for the van der Waals interaction in literatures. The reported theoretical values[6,8,12] for D_o are in the range of -183.51~-160.01 cm^{-1}, and the experimental value[26] is -166 cm^{-1}. Our value is slightly lower than the experimental one but has certainly a comparable accuracy with other theoretical values. Since the well depth of Ar + CO_2 interaction potential (D_e) used is 9.359×10^{-4} au (=205.4 cm^{-1}), the zero point energy turns out to be 33.3 cm^{-1}.

The first excited vibrational state that lies higher by 24 cm^{-1} than the ground (0,0,0) state is the van der Waals bending state (0,0,1). And the next state is the van der Waals stretching (0,1,0) state which is higher by 37 cm^{-1} than the ground state. From this we are able to understand the vibrational motion of Ar-CO_2, *i.e.*, the Ar atom moves inwards and outwards against CO_2 with large amplitude while the bending motion of Ar atom is rather tight. For the excited vibrational levels of Ar-CO_2, we can not find any reported values to compare with.

The "van der Waals (vdW) energy" can be defined as the energy difference between the energy of free CO_2($\upsilon' = \upsilon_1$) and that of Ar-CO_2(υ_1, υ_2, υ_3). The calculated vdW bond

Table 1. The energy levels (cm^{-1}) of the symmetric stretching vibration (υ') of CO_2. Experimental data are from Ref. 35.

υ'	This work	Experimental	Difference
0	-147187.23	-147187.09	-0.14
1	-145839.83	-145839.22	-0.61
2	-144498.99	-144497.55	-1.44
3	-143164.71	-143162.08	-2.63
4	-141836.98	-141832.81	-4.17
5	-140515.80	-140509.74	-6.06
6	-139201.14	-139192.87	-8.27
7	-137893.01	-137882.20	-10.81
8	-136591.40	-136577.73	-13.67
9	-135296.30	-135279.46	-16.84
10	-134007.71	-133987.39	-20.32

Table 2. Vibrational energy levels (cm^{-1}) of CO_2 and Ar-CO_2. The zero of energy is the υ'=0 ground symmetric stretching state of CO_2.

υ'/υ_1	$CO_2(\upsilon')$	Ar-$CO_2(\upsilon_1,0,0)$	Ar-$CO_2(\upsilon_1,0,1)$	Ar-$CO_2(\upsilon_1,1,0)$
0	0.00	-172.07	-147.95	-134.69
1	1347.40	1175.35	1199.45	1212.72
2	2688.24	2516.20	2540.29	2553.56
3	4022.52	3850.49	3874.57	3887.85
4	5350.25	5178.23	5202.30	5215.58
5	6671.43	6499.43	6523.49	6536.78
6	7986.09	7814.09	7838.15	7851.44
7	9294.22	9122.24	9146.28	9159.57
8	10595.83	10423.86	10447.89	10461.19
9	11890.93	11718.97	11742.99	11756.30
10	13179.52	13007.59	13031.59	13044.90
11	14461.63	14289.71	14313.70	14327.02
12	15737.25	15565.34	15589.32	15602.65

energies in cm^{-1} are, for example, 172.07 for the Ar-CO_2(0,0,0) state, 147.96 for (0,0,1), 134.69 for (0,1,0), 172.05 for (1,0,0), 172.04 for (2,0,0), 172.00 for (5,0,0), and 171.93 for (10, 0,0), etc. As the states go higher, the vdW energy gradually decreases. It obviously suggests that the weaker van der Waals bond at highly excited states may easily dissociate.

The vibrational predissociation of Ar-CO_2 can be considered as the following reaction, *i.e.*, Ar-$CO_2(\upsilon_1', \upsilon_2', \upsilon_3')$ → Ar-$CO_2(\upsilon_1, \upsilon_2, \upsilon_3)$ → $CO_2(\upsilon')$ + Ar. The first step is the very fast absorp-tion process of radiation, for example, infrared. The Ar-CO_2 at the initial $(\upsilon_1', \upsilon_2', \upsilon_3')$ state absorbs the photon energy and excites to the $(\upsilon_1, \upsilon_2, \upsilon_3)$ state. Then the Ar-CO_2 in the excited state undergoes spontaneous dissociation to the fragments of CO_2 and Ar. This predissociation widens the homogeneous linewidth of absorption peak. The second step is relatively slow so that it determines the overall rate of dissociation. Therefore in this work only the latter step is considered (the so called half-collision model). Of course, also note that we consider only the υ_1 vibrational modes, *i.e.*, the symmetric stretching motions of CO_2.

When $\upsilon' = \upsilon_1 - 1$, it will be called the $\Delta\upsilon = -1$ process. Likewise, the $\Delta\upsilon = -2$ process is when $\upsilon' = \upsilon_1 - 2$, and so on. For the predissociation process of $\Delta\upsilon = -1$, it can be viewed as follows. The vibrational relaxation of Ar-$CO_2(\upsilon_1,0,0)$ occurs to the state of $(\upsilon_1-1,0,0)$ and the energy released from the relaxation may break the vdW bond of Ar-$CO_2(\upsilon_1-1,0,0)$. The excess energy, which is left over from breaking the bond, flows into the internal rotational motion of product $CO_2(\upsilon' = \upsilon_1 - 1)$ and the translational of CO_2 and Ar. This is so called intramolecular V → T process.

The calculated energy difference between Ar-CO_2(1,0,0) and Ar-CO_2(0,0,0) is 1347.40 cm^{-1} which is larger than the vdW energy, 172.07 cm^{-1} of Ar-CO_2(0,0,0). Therefore the vibrational predissociation of Ar-CO_2(1,0,0) → CO_2(0) + Ar spontaneously occurs. The same is true for any other $(\upsilon_1,0,0)$ or $(\upsilon_1, \upsilon_2, \upsilon_3)$ states as long as the vibrational relaxation energy is greater than the vdW bond energy. It is also true for the process of $\Delta\upsilon = -2, -3$, etc.

Table 3. Vibrational predissociation rates (10^6 s^{-1}), lifetimes (10^{-6} s), and absorption linewidths (10^{-6} cm^{-1}) for the vibrational predissociation of Ar-$CO_2(\upsilon_1,0,0)$ → $CO_2(\upsilon_1-1)$ + Ar. υ_1 indicates the symmetric stretching vibrational mode of CO_2

υ_1	Rate	Lifetime	Linewidth
1	0.36	2.81	1.89
2	0.74	1.36	3.91
3	1.14	0.88	6.06
4	1.57	0.64	8.36
5	2.03	0.49	10.80
6	2.52	0.40	13.39
7	3.04	0.33	16.14
8	3.59	0.28	19.06
9	4.17	0.24	22.15
10	4.79	0.21	25.41
11	5.44	0.18	28.87
12	6.12	0.16	32.51

The predissociation rates, lifetimes, and FWHM (full width at half maximum) linewidths of absorption peaks are listed in Table 3 for the low $(\upsilon_1,0,0)$ states for $\Delta\upsilon = -1$ process. The rates for $\Delta\upsilon = -2$ process are the 6th order of magnitude smaller than those for the corresponding $\Delta\upsilon = -1$ process, which can be practically ignored when the vibrational predissociation from the lower vibrational level of Ar-CO_2 is of interest. The rates for $\Delta\upsilon = -3$ process are virtually zero. The dissociation rates increase as the υ_1 level increases. The vibrational energy gap between two adjacent levels decreases as the υ_1 increases. Therefore the vibrational relaxation into a lower level becomes much easier (energy gap law) to increase the dissociation rate.

As shown in Figure 2, accordingly the lifetime of the transient Ar-$CO_2(\upsilon_1,0,0)$ decreases as the υ_1 increases, *i.e.*, the highly excited states are less stable. The lifetimes are in the order of microseconds (10^{-6} s), for example, 2.81 μs for (1,0,0). They are much longer than those for halogen atom-diatom van der Waals complexes. It is partly because the vdW binding energy for Ar-CO_2 is large. Nonetheless the lifetime seems to be extraordinarily long. We want to stress that, in this work, we considered only the relaxation from a symmetric stretching to another symmetric stretching mode of CO_2. But, in reality, there are antisymmetric stretching and bending motions in CO_2 so that the relaxation from a symmetric stretching level to an antisymmetric stretching or a bending level is possible. If the neglected modes are included in calculations, it is certain that the lifetimes become shorter. Therefore our lifetimes might be regarded as the upper bound. Experimental estimation of lifetime was once reported to be in the order of 50 ns.[26] We have calculated rates, linewidths, lifetimes, and rotational state distributions of product for many Ar-CO_2 initial states and CO_2 final states. But, in the present paper, only partial data are reported to save the space. Full data can be obtained from

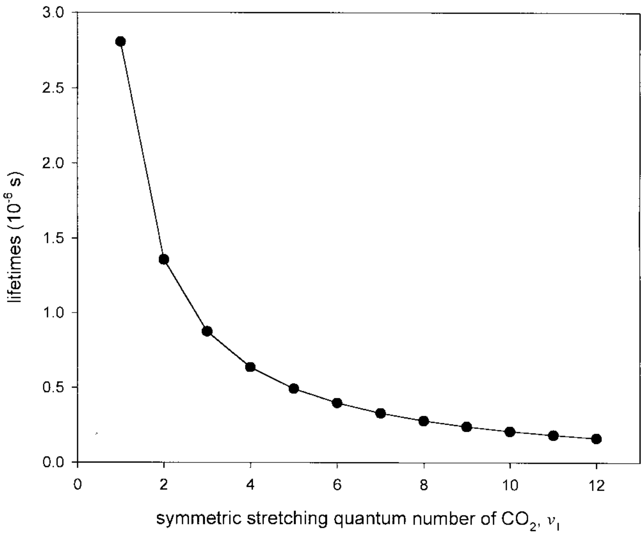

Figure 2. Predissociation lifetimes (10^{-6} s) of the transient Ar-CO_2 $(\upsilon_1,0,0)$. The antisymmetric stretching and bending states of CO_2 are excluded.

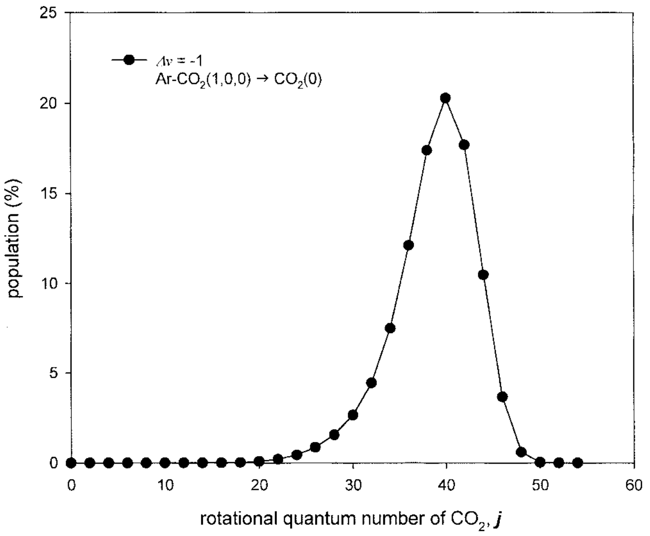

Figure 3. Rotational state distributions of $CO_2(0)$ product from the Ar-$CO_2(1,0,0)$ vibrational predissociation.

the authors.

The rotational state distributions of the diatomic fragment of CO_2 are presented in Figure 3 for the dissociation of Ar-$CO_2(1,0,0) \rightarrow CO_2(0)$ + Ar. The distribution shows a prominent maximum peak at rather high rotational state. The CO_2 in either low *j* states or high *j* states are not produced from the predissociation of Ar-CO_2. For higher υ_1 states, *i.e.*, $\upsilon_1>1$, the same pattern is found. This feature is somewhat different from other cases of predissociation. The frequently found rotational state distributions of the diatom product from the vibrational predissociation of atom-diatom van der Waals complex are two types; one is that the lowest *j* state populates most and the population gradually decreases as *j* goes higher, and the other is the case of bimodal distribution. Ar-CO_2 has, even at the vibrational state of (1,0,0), has relatively large vdW bending zero point energy so that the outcoming CO_2 may have a lot of rotational energy. But, at the same time, Ar-CO_2 has a vdW stretching zero point energy which can be directly transferred to the translational energy of the product CO_2. The competition of the two types of vdW vibrational motions may compete. It accounts for the existence of the maximum in rather high *j* state. However, in order to fully understand the rotational state distributions, more studies on various atom-triatom systems will be necessary.

Summary and Conclusions

A new and simple Morse type potential energy function for Ar-CO_2 is suggested. The suggested potential function is as accurate as already known potential energy functions but it exclusively includes the dependence of the potential energy on the CO_2 symmetric stretching vibrational coordinates. With the potential energy function the VSCF-DWB-IOS approximate theoretical method has been applied to the vibrational predissociation of Ar-CO_2. The dissociation rates, absorption linewidths, lifetimes of transient excited Ar-CO_2 species, and rotational distributions of the product CO_2 are all computed. The self-consistent field (VSCF) calculations have revealed detailed and rich vibrational structures of Ar-CO_2, *i.e.*, many van der Waals stretching and bending vibrational levels exist. The VSCF method is found to reproduce the ground vibrational level accurately. For the excited states, the accuracy of the method could not be tested because no experimental values are available. The distorted-wave Born (DWB) and the infinite-order sudden (IOS) approximations seem not to impose serious problems.

We verified that the symmetric stretching mode of CO_2 can be effectively coupled with the van der Waals vibrational modes, which can bring the vibrational predissociation of Ar-CO_2. The lifetime of Ar-$CO_2(1,0,0)$ is calculated to be in the order of a microsecond. The rotational state distributions of the product $CO_2(\upsilon')$ are found to be independent of symmetric stretching υ' mode, and high rotational states are rather heavily populated. Generally the dissociation rates are found to be small. It is probably due to the neglect of the coupling of the symmetric stretching mode with the antisymmetric stretch and bending modes in CO_2. Full calculations including all the four vibrational modes of CO_2 will be pursued in the near future.

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References

1. Rohrbacher, A.; Halberstadt, N.; Janda, K. C. *Ann. Rev. Phys. Chem.* **2000**, *51*, 405.
2. Parker, G. A.; Snow, R. L.; Pack, R. T. *J. Chem. Phys*. **1976**, *64*, 1668.
3. Preston, R. K.; Pack, R. T. *J. Chem. Phys*. **1977**, *66*, 2480.
4. Hough, A. M.; Howard, B. J. *J. Chem. Soc. Faraday Trans.* **1987**, *83*, 173.
5. Roche, C. F.; Ernesti, A.; Hutson, J. M. *J. Chem. Phys*. **1996**, *104*, 2156.
6. Marshall, P. J.; Szczesniak, M. M.; Sadlej, J.; Chalasinski, G.; ter Horst, M. A.;. Jameson, C. J. *J. Chem. Phys*. **1996**, *104*, 6569.
7. ter Horst, M. A.; Jameson, C. J. *J. Chem. Phys*. **1996**, *105*, 6787.
8. Hutson, J. M.; Ernesti, A.; Law, M. M.; Roche, C. F.; Wheatly, R. J. *J. Chem. Phys*. **1996**, *105*, 9130.
9. Rak, J.; Szczesniak, M. M.; Chalasinski, G.; Cybulski, S. M. *J. Chem. Phys*. **1997**, *106*, 10215.
10. Roche, C. F.; Dickinson, A. S.; Ernesti, A.; Hutson, J. M. *J. Chem. Phys*. **1997**, *107*, 1824.
11. Thibault, F.; Boissoles, J.; Boulet, C.; Ozanne, L.; Bouanich, J. P.; Roche, C. F.; Hutson, J. M. *J. Chem. Phys*. **1998**, *109*, 6338.
12. Misquitta, A. J.; Bukowski, R.; Szalewicz, K. *J. Chem. Phys*. **2000**, *112*, 5308.
13. Boulet, C.; Isnard, P.; Arie, E. *J. Quant. Spectrosc. Radiat. Transf.* **1974**, *14*, 637.
14. Herpin, M. C.; Lallermand, P. *J. Quant. Spectrosc. Radiat. Transf.*

1975, *15*, 779.
15. Meyer, T. W.; Rhodes, C. K.; Haus, H. A. *Phys. Rev. A* **1975**, *12*, 1993.
16. Loesch, H. J. *Chem. Phys*. **1976**, *13*, 431.
17. Steed, J. M.; Dixon, T. A.; Kelmperer, W. *J. Chem. Phys*. **1979**, *79*, 4095.
18. Bulanin, M. O.; Bulychev, V. P.; Khodos, E. B. *Opt. Spectrosc.* **1980**, *48*, 403.
19. Kalinim, A. P.; Khromov, V. N.; Leonas, V. R. *Mol. Phys*. **1982**, *47*, 811.
20. Jameson, C. J.; Jameson, A. K.; Smith, N. C.; Jackowski, K. *J. Chem. Phys*. **1987**, *86*, 2717.
21. Randall, R. W.; Walsh, M. A.; Howard, B. J. *Faraday Symp. Chem. Soc.* **1988**, *85*, 13.
22. Fraser, G. T.; Pine, A. S.; Suenram, R. D. *J. Chem. Phys*. **1988**, *88*, 6157.
23. Sharpe, S. W.; Reifschneider, D.; Wittig, C.; Beaudet, R. A. *J. Chem. Phys*. **1991**, *94*, 233.
24. Margottin-Maclou, M.; Henry, A.; Valentin, A. *J. Chem. Phys*. **1992**, *96*, 1715.
25. Thibault, F.; Boissoles, J.; Le Doucem, R.; Bouanich, J. P. *J. Chem. Phys*. **1992**, *96*, 4945.
26. Bohac, E. J.; Marshall, M. D.; Miller, R. E. *J. Chem. Phys*. **1992**, *97*, 4890.
27. Bohac, E. J.; Marshall, M. D.; Miller, R. E. *J. Chem. Phys*. **1992**, *97*, 4901.
28. Brownsword, R. A.; Salh, J. S.; Smith, I. W. M. *J. Chem. Soc. Faraday Trans*. **1995**, *91*, 191.
29. Mader, H.; Heineking, N.; Stahl, W.; Jager, W.; Xu, Y. *J. Chem. Soc. Faraday Trans.* **1996**, *92*, 901.
30. Ceotto, M.; Garcia-Vela, A. *J. Chem. Phys*. **2001**, *115*, 2146.
31. Seong, J.; Sun, H.; Schatz, G. C.; Ratner, M. A.; Gerber, R. B. *J. Phys. Chem. A* **1998**, *102*, 9345.
32. Jung, J.; Sun, H. *Chem. Phys. Lett*. **2001**, *336*, 311.
33. Jung, J.; Sun, H. *Mol. Phys.* **2001**, *99*, 1867.
34. Wright, N. J.; Gerber, R. B. *J. Chem. Phys*. **2001**, *114*, 8763.
35. Suzuki, I. *J. Mol. Spectrosc.* **1968**, *25*, 479.
36. Herzberg, G. *Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1950.
37. Cybulski, S. M.; Kendall, R. A.; Chalasinski, G.; Severson, M. W.; Szczesniak, M. M. *J. Chem. Phys*. **1997**, *106*, 7731.