VIBRATIONAL WAVE PACKET GENERATION AND TIME EVOLUTION IN DIATOMIC IONS

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A theoretical calculation of the generation and the time evolution of vibrational wave packets in diatomic ions is described. Under the irradiation of a short laser pulse, the alkali–rare gas van der Waals molecule may undergo photoionization and the ground state vibrational wavepacket is set up at the resulting alkali–rare gas ion potential. The temporal behavior and the spontaneous emission of the wave packets are described. The effect of the vibrationally and rotationally excited states of the initial electronic ground state on the dispersion of the generated total vibrational wave packet is also discussed.

1. Introduction

Recent advances in the observation of the time evolution of the molecular photodissociation process [1–3] and the time-dependent spectrum originating from the resonant excitation of the entire vibronic manifold of the ground electronic state to some excited electronic state [4] have generated great interests in the dynamics of the molecular wave packets. These studies rekindle the general interest in the theoretical aspects of the wave packet dynamics, especially in the vibrational motion of nuclei in the electronic potentials [5–7]. Historically, it was Schrödinger [8] who first realized the classical dynamic behavior of Gaussian wave packets in the harmonic oscillator (HO). As far as the dynamics of the wave packets in one-dimensional potentials is concerned, various forms of wave packets have been constructed and tested in general potentials by Nieto and co-workers [9]. The relationship between the classical motion and the minimum uncertainty coherent states was also discussed [9]. Basing on the dynamics of Gaussian wave packets, several groups have developed time-dependent theories for the processes of photodissociation and Raman light scattering [10,11].

In the above studies, the Gaussian coherent states were used either as a basis set in describing the physical processes or as an experimentally generated

idealized state. In most cases, such as the pumping of the ground vibrational manifold to an excited electronic state by an ultrafast laser pulse, a general mixed-state wave packet instead of a Gaussian coherent state is generated. Up to date the reported studies are mainly concentrated on the bound discrete electronic states. In this paper we report theoretical calculations on the generation of vibrational wave packets in M^+Rg diatomic ions through the photoionization of MRg van der Waals molecules. Here M represents the alkali atoms and Rg the rare gas atoms. The time evolution and the spontaneous photon emission rate of the wave packets are also reported. The effects of the vibrationally and rotationally excited states on the dynamics of the wave packets are also discussed. This study opens another experimental possibility in investigating the fundamental properties of wave packets.

2. Generation of the vibrational wave packets in diatomic ions

Let us consider the van der Waals molecules formed between alkali atom M and rare gas Rg . Under the irradiation of a short laser pulse, the system MRg may undergo a single-photon ionization process. We shall limit the present discussion to the photoionization of the valence electron of M . Fig. 1 shows the adiabatic

Fig. 1. Relative position of NaXe and Na⁺Xe adiabatic potentials adapted from refs. [12,13]. The arrow at 4.95 Å indicates the minimum position of NaXe.

potentials of NaXe and Na⁺Xe, a typical MRg and M⁺Rg system. The general relative positions of the potential minima of MRg and M⁺Rg are quite similar among the alkali-rare gas van der Waals molecules.

The Hamiltonian of the molecular system, H_m , plus the molecule-electromagnetic interaction, H_{int} , may be expressed as

$$H = H_m + H_{int}. \quad (1)$$

Neglecting the molecular rotation term, a point to be discussed later, and under the Born-Oppenheimer approximation, the initial state may be written as

$$|0, N\rangle = |0\rangle |N\rangle, \quad (2)$$

where $|0\rangle$ is the ground vibrational state supported by the N -electron adiabatic potential with electronic wavefunction $|N\rangle$. The final states are

$$|v, N-1, \mathbf{p}\rangle = |v\rangle |N-1\rangle |\mathbf{p}\rangle, \quad (3)$$

where $|v\rangle$ covers the range of the final vibrational states supported by the $(N-1)$ -electron adiabatic

potential with an electronic wavefunction of $|N-1\rangle$ and $|\mathbf{p}\rangle$ is the wavefunction of the ionized electron with linear momentum $\mathbf{p}$. Since we are not considering the possible molecular dissociation accompanied by the photoionization, the v values are assumed to be discrete. In later calculations we shall see that this is a very good approximation for MRg systems.

In the interaction picture, and neglecting the coupling between the continuum states $|\mathbf{p}\rangle$, the time evolution of the system is governed by the following first-order differential equations:

$$\begin{aligned} \dot{C}_{vp}(t) = & -\frac{i}{\hbar} \langle v, N-1, \mathbf{p} | H_{int}(t) | 0, N \rangle \\ & \times \exp[i(\omega_p + \omega_v)t] C_0, \end{aligned} \quad (4)$$

$$\begin{aligned} \dot{C}_0(t) = & -\frac{i}{\hbar} \int \sum_v \langle v, N-1, \mathbf{p} | H_{int}(t) | 0, N \rangle \\ & \times \exp[-i(\omega_p + \omega_v)t] C_{vp} d\mathbf{p}, \end{aligned} \quad (5)$$

where C_0 and C_{vp} are the time-dependent coefficients of $|0, N\rangle$ and $|v, N-1, \mathbf{p}\rangle$, respectively. The state of zero energy is set at $|0, N\rangle$ and the vibrational energy is designated as the energy supported by the electronic adiabatic potential. One also notes that $\omega_p \gg \omega_v$ in the present consideration.

In the rotating wave approximation and under the assumption of weak energy dependence of the bound-free matrix elements, the first-order perturbation solution of $C_{vp}(t)$ is

$$\begin{aligned} C_{vp}(t) = & -\frac{i}{\hbar} \int_0^t \langle v, N-1, \mathbf{p} | H_{int}(t') | 0, N \rangle \\ & \times \exp[i(\omega_p + \omega_v)t'] dt'. \end{aligned} \quad (6)$$

The final photoionized state is

$$\begin{aligned} |\psi_f(t)\rangle = & \int \sum_v \left[-\frac{i}{\hbar} \left(\int_0^t E(t') \cdot F_{i\omega} D_p \right. \right. \\ & \times \exp[i(\omega_p + \omega_v)t'] dt' \Big) \\ & \times \exp[-i(\omega_p + \omega_v)t] |v, N-1, \mathbf{p}\rangle \Big] d\mathbf{p}, \end{aligned} \quad (7)$$

where

$$\langle v, N-1, \mathbf{p} | H_{\text{int}}(t) | 0, N \rangle = \mathbf{E}(t) \cdot F_{v0} \mathbf{D}_p,$$

$$\mathbf{D}_p \equiv \langle N-1, \mathbf{p} | -\sum \mathbf{e} r_i | N \rangle,$$

$$F_{v0} \equiv \langle v | 0 \rangle,$$

and $\mathbf{E}(t)$ is the electric field.

Expressing the laser field in the frequency domain, the time integral of eq. (7) becomes

$$\begin{aligned} & \int_0^t \mathbf{E}(t') \exp[i(\omega_p + \omega_v)t'] dt' \\ &= \int \mathbf{a}(\omega) \frac{1 - \exp[i(\omega_p + \omega_v - \omega)t]}{i(\omega_p + \omega_v - \omega)} d\omega, \end{aligned} \quad (8)$$

where $\mathbf{a}(\omega)$ is the laser field amplitude at ω . Under the condition

$$t \gg \frac{1}{\omega_p + \omega_v} \quad (9)$$

one obtains the approximation [14]

$$\begin{aligned} & \frac{1 - \exp[i(\omega_p + \omega_v - \omega)t]}{i(\omega_p + \omega_v - \omega)} \\ & \approx \pi \delta(\omega_p + \omega_v - \omega) - iP \frac{1}{\omega_p + \omega_v - \omega}, \end{aligned} \quad (10)$$

where P represents the Cauchy principal value.

Substituting eqs. (9) and (10) into eq. (7), one obtains

$$\begin{aligned} |\psi_f(t)\rangle &= \frac{i\pi}{\hbar} \sum_v \int \mathbf{a}(\omega_p + \omega_v) \cdot F_{v0} \mathbf{D}_p \\ & \times \exp[-i(\omega_p + \omega_v)t] |v, N-1\rangle |p\rangle d\mathbf{p} \\ & + \text{principal value part.} \end{aligned} \quad (11)$$

The Cauchy principal value of eq. (10) is an odd function with respect to ω and would only cause the shift of the energy levels in one-photon process in eq. (11) [14].

In the case that the mean photon energy is well above the ionization threshold and the photon field is short enough such that the band width of the laser field is much wider than the band width of ω_v allowed by the Franck-Condon factors, one may neglect the contribution of the principal value part and take the approximation

$$\begin{aligned} \mathbf{a}(\omega_p + \omega_v) &= \mathbf{a}(\omega_p + \bar{\omega}_v) \\ &+ \mathbf{a}'(\omega_p + \bar{\omega}_v) \Delta\omega + \dots, \end{aligned} \quad (12)$$

where $\bar{\omega}_v$ is the average value of ω_v allowed by the Franck-Condon principle, and one obtains the first approximation term of the final photoionized state

$$\begin{aligned} |\psi_f(t)\rangle & \approx -\frac{i\pi}{\hbar} \left(\sum_v F_{v0} \exp(-i\omega_v t) |v, N-1\rangle \right) \\ & \times \int \mathbf{a}(\omega_p + \bar{\omega}_v) \cdot \mathbf{D}_p \exp(-i\omega_p t) |p\rangle d\mathbf{p} \end{aligned} \quad (13)$$

($\mathbf{a}'$ is the first derivative of $\mathbf{a}$). The above conditions exclude the threshold behavior in our calculation.

The vibrational wavefunction would evolve according to

$$|\psi_f^{\text{vib}}(t)\rangle = \sum_v F_{v0} \exp(-i\omega_v t) |v, N-1\rangle. \quad (14)$$

In the limit of time zero, one recovers the ground state vibrational wavefunction,

$$\lim_{t \rightarrow 0} |\psi_f^{\text{vib}}(t)\rangle = |0, N\rangle. \quad (15)$$

The final results can be simply stated as follows: in the sudden approximation, the vibrational wavefunction of the initial ground electronic state evolves in the final ionic adiabatic potential after the photoionization. In the above analysis, we have tacitly neglected the coupling between the valence electron and the core electrons. The photoionization efficiency is assumed to be constant in the wavelength region we considered. The momentum recoil process of the ionized electron was also not taken into account. One should also note that there is a conceptual resemblance between the analysis of the atomic inner shell ionization process [15,16] and the analysis of the present results. The advances of laser technology in the pico- and femtosecond time domain [1-4], and the ability to generate van der Waals molecules in supersonic jet expansions [17], open the possibility for experimental studies of these calculations.

3. The time evolution of the vibrational wave packets

In this section, we shall study the time evolution of

the wave packets, especially those of the ground state harmonic oscillator (HO) and Morse oscillator (MO) wavefunctions in real potentials. As mentioned previously, the general systems are MRg and M^+Rg and the specific system is NaXe and Na^+Xe .

The continuum contribution of the ground state wave packet in the ionic potential may be estimated by the energy dispersion of the wave packet in the ionic Hamiltonian. Let H_{ion} and H_{neu} represent the Hamiltonians of the nuclear motion in the ionic and neutral van der Waals potentials, respectively, and χ_0 be the eigenfunction of H_{neu} ,

$$\begin{aligned} H_{ion} &= \frac{p'^2}{2\mu'} + V_{ion}(R), \\ H_{neu} &= \frac{p^2}{2\mu} + V_{neu}(r), \end{aligned} \quad (16)$$

where μ, μ' and p, p' are the reduced mass and atomic linear momentum of the neutral and ionic species, respectively. Neglecting the kinetic energy of the electron moving in the velocity of the center of mass, the energy dispersion of χ_0 in the ionic potential is

$$\begin{aligned} \langle \Delta H \rangle^2 &= \langle H_{ion}^2 \rangle - \langle H_{neu} \rangle^2 \\ &\approx \langle \Delta V^2 \rangle - \langle \Delta V \rangle^2, \end{aligned} \quad (17)$$

with $\Delta V = V_{ion} - V_{neu}$.

For the M^+Rg systems, we can estimate the energy dispersion of the wave packet analytically. The wave packet can be approximated by a Gaussian form with position at R_0 and a spatial dispersion of σ^2 . ΔV is approximated by the ion-induced dipole potential of $-\alpha/2R^4$ for $R > R_{min}$ and a mean finite value of δ for $R < R_{min}$. Here R_{min} is the position of the minimum potential of M^+Rg and α is the electric polarizability of Rg. One obtains

$$\begin{aligned} \langle \Delta V^2 \rangle &= \frac{\sigma\alpha^2}{4} \sqrt{\frac{2}{\pi}} \int_{R_{min}}^{\infty} \frac{1}{R^8} \\ &\quad \times \exp[-2\sigma^2(R-R_0)^2] dR + \delta_1, \\ \langle \Delta V \rangle &= -\frac{\sigma\alpha}{2} \sqrt{\frac{2}{\pi}} \int_{R_{min}}^{\infty} \frac{1}{R^4} \\ &\quad \times \exp[-2\sigma^2(R-R_0)^2] dR + \delta_2, \end{aligned} \quad (18)$$

where $\sigma^2 = 1.4830126 \times 10^2 \omega_e \mu_{MRg}$ with the vibrational frequency of MRg, ω_e , in units of cm^{-1} and the

reduced mass of MRg, μ_{MRg} , in units of amu. R_0 is the minimum energy position of MRg in Å. δ_1 and δ_2 are the integral values between 0 and R_{min} .

Since the Gaussian wave packet is localized around R_0 , one may use the asymptotic expansion method to evaluate the integrals and obtain the leading term of the energy uncertainty,

$$\Delta H \equiv \sqrt{\langle \Delta H \rangle^2} \approx \frac{\alpha}{2R_0^4} \frac{2}{R_0\sigma}, \quad (19)$$

where $\alpha/2R_0^4$ is just the ion-induced dipole interaction.

For the NaXe case, eq. (19) becomes

$$\Delta H_{NaXe} = 0.177 \frac{\alpha_{Xe}}{2R_0^4}. \quad (20)$$

Comparing eq. (20) with the ion-induced dipole interaction, the continuum contribution is less than 0.01% in the approximation of the normal distribution. The other MRg systems have the similar properties.

Following the analysis of section 2, the vibrational wave packet is governed by the time-dependent Schrödinger equation,

$$i\hbar \frac{\partial \chi}{\partial t} = H_{ion} \chi. \quad (21)$$

Two numerical procedures were used to solve the equation. For the time evolution of the wave packet, the direct integration method developed by Goldberg et al. [18] was used. For the confirmation of the confinement of the generated wave packet within the ionic bound state, the eigenenergies and eigenfunctions of the ionic states were firstly solved by the Numerov-Cooley method [19,20]. The wave packets were then expanded on these bases and the percentage of the continuum contribution can be calculated.

For the NaXe and Na^+Xe systems, the ground state NaXe potential has been obtained by Okel and van de Ree [12] using atomic beam scattering technique. The ground state Na^+Xe potential has been calculated by Waldman and Gordon [18]. Fig. 1 shows the relative position of these two adiabatic potentials.

Using the Dunham procedure [21], the vibrational spectroscopic constants, ω_e and $\omega_e x_e$, of NaXe were calculated from the ground state potential. The vibrational wavefunction was then approximated by

two kinds of wave packets calculated from these spectroscopic data: harmonic oscillator (HO) and Morse oscillator (MO) ground state wavefunctions.

Fig. 2 shows how the HO wave packet of NaXe evolves in the Na⁺Xe ionic potential after the photoionization. The mean energy of the wave packet is -416 cm^{-1} (zero-point energy is set at dissociation state) and the energy dispersion is 76 cm^{-1} . These values are consistent with the estimated values of eq. (20). The classical period at this energy is 0.810 ps. The uncertainty product of the position and momentum of the initial wave packet is found to be $0.4998\hbar$, which is slightly less than the minimum value allowed by the Heisenberg uncertainty principle. This is attributed to having neglected the momentum recoil process of the ionized electron. As time proceeds, the wave packet starts to disperse immediately.

For the MO wave packet, the mean energy and energy dispersion are -392 and 72 cm^{-1} , respectively. The uncertainty product of the position and momentum is $0.51\hbar$, and is slightly larger than the minimum $0.5\hbar$. The classical period of the vibrational motion is 0.840 ps, and is slightly longer than that of the HO wave packet because of the higher mean energy of the MO wave packet.

The wave packet is initially set up at the classical outer turning point and propagates toward the inner turning point and oscillates between these two turning points. Around the inner turning point, the repulsive wall disperses the wave packet considerably. There is only a limited extent of localization in this region. In the final stage of the first classical period, the wave packet refocuses back partially at the outer turning point. The spatial localization of the wave packet essentially disappears in a few classical periods.

Since we are considering a coherent state and also because the eigenstates involved are finite in number, the long time wave packet recurrence is bound to occur. Following the argument proposed by Parker and Stroud [22] the vibrational wave packet may be represented by

$$\begin{aligned}\chi(t) &= \sum_n b_n(R) \exp\left(\frac{-iE_n t}{\hbar}\right) \\ &= \exp\left(-\frac{i\bar{E}t}{\hbar}\right) \sum_n b_n(R) \exp\left\{-\frac{it}{\hbar} \left[\Delta' (n - \bar{n}) \right. \right. \\ &\quad \left. \left. + \left(\frac{1}{2!}\right)(n - \bar{n})^2 \Delta'' + \dots \right] \right\},\end{aligned}\quad (22)$$

where E_n is the eigenenergy, b_n is the coordinate amplitude at E_n , $\bar{E}$ is the average energy of the wave packet, $\bar{n}$ is the average vibrational quantum number at $\bar{E}$, and Δ' and Δ'' are the first and second derivatives of the energy spectrum with respect to the vibrational quantum number at $\bar{n}$.

The classical period is $T_0 = \hbar/\Delta'$, and the first long time recurrence period is $T_1 = \hbar/\Delta''$. The higher-order terms can be obtained accordingly. For a pure ion-induced dipole interaction, the eigenenergy spectrum is [23]

$$E(n) = D - X_0(n_D - n)^4, \quad (23)$$

where D , X_0 and n_D are constants. The series of eq. (22) is then cut off after the fifth derivative of eq. (23). A return almost to its initial wave packet form is possible for these systems. This behavior is a general property of the wave packet in a system of eq. (23), no matter whether the wave packet is a HO or a MO wave packet or other well-behaved general wave packets.

For a further looking into the validity of eqs. (22) and (23), we consider the specific system of Na⁺Xe. The eigenenergy spectrum was firstly solved numerically for the full potential of fig. 1. Through the well-known fitting method of ref. [23], it was found that for vibrational quantum number larger than 15 the vibrational motion is essentially following eq. (23). Straightforward calculations show that the prediction of eqs. (22) and (23) is in good agreement with the full quantum mechanical calculation described in the previous sections despite the fact that the medium- and short-range interaction is not a strict ion-induced dipole interaction. This observation also demonstrates the important role the eigenenergy spectrum plays in the dynamics of the wave packet.

Fig. 2. (a)–(c) show the time evolution of harmonic oscillator wavepacket in the first classical cycle. The system is Na^+Xe and the classical period is 0.810 ps. Each consecutive number in (a)–(c) represents a time interval of 0.1013 ps, one eighth of the classical period.

4. The spontaneous emission of the vibrational wave packets

The electric dipole moment of M^+Rg is

$$u = - \sum_i e y_i + Z_M e y_M + Z_{\text{Rg}} e y_{\text{Rg}}, \quad (24)$$

where $-e$ is the charge of the electron; Z_M and Z_{Rg} are the atomic numbers of M and Rg, respectively; and y_i , y_M , and y_{Rg} are the coordinates of the electrons, M nucleus and Rg nucleus, respectively. Since M^+ and Rg both have electronic closed-shell structures, the dipole moment in the low frequency regime originating from the nuclear motion may be approximated by [24]

$$u = \frac{e m_{\text{Rg}}}{m_{\text{tot}}} R, \quad (25)$$

where m_{Rg} and m_{tot} are the masses of Rg and the M^+Rg ion, R is the relative displacement from Rg to M^+ . Because the internal states of the ions are involved in the radiative transition, the origin of the system should be set at the center of mass [24]. Judging from the variation of the induction force coefficient with respect to the internuclear distance R [25], eq. (25) is a good approximation over the range of the vibrational discrete states.

The total spontaneous emission power of the vibrating ion M^+Rg may be calculated from the expectation value of the dipole operator [26],

Fig. 3. Intensity of the spontaneous emission of the harmonic oscillator wave packet in Na^+Xe ionic potential. The first long time recurrence appears at 10.8 ps.

$$P(t) = \frac{4e^2 m_{\text{Rg}}^2}{3C^3 m_{\text{tot}}^2} \langle \chi | : \ddot{\mathbf{R}} \cdot \ddot{\mathbf{R}} : | \chi \rangle, \quad (26)$$

where χ is the vibrational wavefunction at the end of the laser pulse, and $\ddot{\mathbf{R}}$ is the acceleration operator of the dipole oscillator. The colons indicate the operator is normally ordered. Since the radiative lifetime is much longer than the classical period of the wave packet, to a good approximation eq. (26) can be written in the form

$$P(t) = \frac{4e^2}{3C^3 m_{\text{M}^+}} \times \langle \chi(t) | \nabla V_{\text{ion}}(\mathbf{R}) \cdot \nabla V_{\text{ion}}(\mathbf{R}) | \chi(t) \rangle, \quad (27)$$

where $\nabla V_{\text{ion}}(\mathbf{R})$ is the gradient of the adiabatic potential of the ion, and $\chi(t)$ is the time-dependent vibrational wavefunction. Fig. 3 shows the total emission power of the Na^+Xe wave packet. As the wave packet approaches the inner repulsive wall, the emission power reaches its peak. The long time recurrence of the wave packet also reflects in the emission profile. For the Na^+Xe case, the first long time recurrence appears at 10.8 ps. Besides the differences in the classical periods, the other M^+Rg systems manifest a similar behavior.

5. The effect of the rotationally and vibrationally excited states on the spreading of the wave packets

Under the conventional preparation methods for the van der Waals molecules, such as the supersonic beam expansion technique, the molecules are usually generated in a mixed state with the rotationally and vibrationally excited states in a certain population distribution. The detail of these distributions is determined by the preparation conditions. During the short photoionization period, a randomly distributed ensemble of molecules is excited. Because of the vast distance between these gas molecules, one could assume the independence of the dynamics of each molecular wave packet. The macroscopic spontaneous emission or other experimental observations could well be described by a statistical summation of the individual molecules. The effect of the rotational and vibrational motions on the dispersion of the vibrational wave packet can be calculated by just looking to the behavior of the individually excited molecules.

In a formal treatment, one could start from a fixed rotational quantum number and set up an effective electronic potential for the vibrational motion. The vibrational wave packet could then be generated and its time-dependent behavior could be solved according to the general scheme discussed in the previous sections. For a complete description, all the allowed rotational and vibrational states should be calculated and the resulting wave packets should be summed up according to their statistical weight. The whole procedure is computer-time consuming and not physically illuminating.

Instead of going into the details of the calculation, one could estimate the effect of the rotationally and vibrationally excited states on the spreading of the ensemble-summing wave packet according to the following observations. The interaction potentials of the neutral species are consistently much weaker than those of the corresponding ionic species. Therefore, even in a vibrationally or rotationally excited state, the wave packet is always generated at the outer attractive branch of the ionic interaction potential whose functional form could be well described by the ion-induced dipole potential. The corresponding eigenenergy spectrum is expressed as eq. (23). With the help of eq. (22), one could estimate the time-de-

pendent behavior of the wave packet reasonably accurately.

In a supersonic expansion, the MRg van der Waals molecules could be generated in a wide range of rotational and vibrational temperature, ranged from a few K to about 40 K [17,27,28]. For the present purpose, we assume that a 5 K rotational temperature and a 10 K vibrational temperature are generated in NaXe van der Waals molecules. The vibrational fundamental frequency of NaXe electronic ground state is 17.9 cm^{-1} [12]. The Boltzmann distribution at the first vibrationally excited state is only 8% with respect to the ground vibrational state at 10 K vibrational temperature. Because the central position of the fundamental and the first vibrational overtone is the same, according to eq. (22), both vibrational wave packets will be set at the same position in the ionic state and the time evolution of the central portion of these two wave packets would be identical. The only difference would be the spreading speed of the vibrational wave packet envelope which is determined by the spread of the vibrational states, i.e. $n - \bar{n}$. The adding of an 8% first vibrational overtone to the fundamental state would not change the general behavior of the total mixed-state vibrational wave packet, except that the wave packet would have a wider energy dispersion and the spreading speed would be faster depending on the relative weight of the vibrationally excited state and the difference of $n - \bar{n}$ between these two vibrational states. The 8% contribution would not appreciably change the dynamics of the present calculation.

For a rotational temperature of 5 K, the maximum-probability rotational quantum number is 7 for the NaXe system. The minimum position of the effective potential would shift 0.0043 Å toward the outer turning point. In other words, the vibrational wave packet would be set up at this new internuclear separation in the ionic state during the photoionization process. For a rotational quantum number of 7 the centrifugal term is comparatively much smaller than the ion-induced dipole interaction at this internuclear distance. The energy spectrum can still be described by eq. (23). An 0.0043 Å shift from 4.95 Å would at most change a few wave numbers of energy in the ionic interaction potential. The dynamics of these wave packets is not expected to be appreciably changed in these rotationally excited states.

6. Discussion and conclusions

The separability between the vibrational motion of the nuclei and the electronic motion of the ionized electron expressed in eq. (13) comes from the pulse excitation of the molecule. In the case of the monochromatic or narrow band excitation, conservation of energy will prevent the separability, and one would only be allowed to consider the composite states of the vibrational plus the electronic motion. According to the generally accepted principles of quantum mechanics [29], any attempt to measure the energy of either one of two spatially separated subsystem would force the other into a definite energy state. As the laser band width becomes narrower than the vibrational band width allowed by the Franck-Condon principle, a separate description of the vibrational wave packets and the electron motion is against the laws of quantum mechanics.

The spontaneous emission of the wave packet is just a specific form of the multilevel emission process and the emission intensity shows the well-known quantum beat behavior [26]. Its detailed structure reveals the energy level spacings involved during the preparation of the wave packet.

There are many diatomic van der Waals molecules, especially those formed from the rare gas atoms and the rest of the elements in the periodic table, which could be photoionized and sustain their ground state vibrational wave packets. The electric dipole moments of the corresponding ions are also most likely to be appreciable because of the different locations of the center of mass and the center of electric charges, except for homonuclear ions, such as Ar_2^+ . Quantum beat behavior is also expected for these systems.

The advantages of studying the alkali-rare gas van der Waals molecules come from the following considerations: first, there is only one valence electron in the system which, having a ionization threshold energy of the order of 5 eV, is experimentally accessible by the present laser technology; second, the final electronic state is well defined, and the other electronic states are all well separated from this state; third, the method for preparing van der Waals molecules has been well established [17] and possible interferences from the other accompanying molecular species, such as alkali atoms, alkali dimers, and rare gases, are ex-

pected to be virtually negligible. However, the direct detection of the fast infrared quantum beat would pose a challenge for the present experimental technology.

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