

Theoretical study of the vibrational-branching ratio and photoelectron angular distribution in $(1+1')$ -photon resonance-enhanced multiphoton ionization of HD and D₂ molecules

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We have studied the isotopic variation of the vibrational-branching ratio (VBR) and the photoelectron angular distribution (PEAD) as a function of laser intensity in $(1+1')$ -photon resonance-enhanced multiphoton ionization (REMPI) of HD and D₂ molecules via $B^1\Sigma_u$ ($v=4; j=1,2$) levels. We have found that with the increase in laser intensity, the non-Franck-Condon nature of the VBR and the deviation of the total as well as the vibrationally resolved PEAD from that obtained in the lower-intensity regime become much more prominent for D₂ molecules than those for HD molecules. We have considered the effect of the interference of different ionization channels (resonant as well as near-resonant ionization via nearby rovibrational levels) and the effect of Raman-like two-photon coupling between these intermediate vibrational levels via a continuum on this REMPI process. The difference between the vibrational wave functions and the difference between the spacing of rovibrational energy levels in these two isotopes of H₂ molecules lead to different strengths of ionization and the Raman-like two-photon coupling. Hence the isotopic variation in the VBR and the PEAD for these two isotopes shows up as a result of different degrees of interference of parallel ionization channels and different strengths of two-photon coupling via a continuum, both of which become important with an increase in laser intensity. We have also found that the intensity variation of the VBR and the PEAD for both molecules depends on the choice of different rotational levels as resonances. This feature has also been found previously in the REMPI of H₂ molecules [Jainab Khatun, S. Sanyal, and Krishna Rai Dastidar, *Phys. Rev. A* **49**, 4765 (1994); Jainab Khatun and Krishna Rai Dastidar, *ibid.* **52**, 2971 (1995), and references therein; J. W. J. Verschuur and H. B. van Linden van den Heuvell, *Chem. Phys.* **129**, 1 (1989)]. [S1050-2947(96)00506-9]

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I. INTRODUCTION

To understand the physical phenomena involved in the resonance-enhanced multiphoton ionization (REMPI) of molecules, theoretical investigation is usually done in simple molecular system such as H₂ or its isotopic variants. Previously, the effect of laser intensity on the vibrational branching ratio (VBR) and the photoelectron angular distribution (PEAD) in $(1+1')$ -photon REMPI of H₂ molecules has been investigated [1,2], considering the effect of near-resonant ionization channels and the effect of higher-order coupling channels. It has been found that with the increase in laser intensity, (i) the interference of ionization channels via different near-resonant vibrational levels and (ii) the two-photon Raman-like transitions between these levels via a continuum can lead to a non-Franck-Condon vibrational distribution and a deviation of the PEAD from that obtained in the lower-intensity regime $\leq 10^8$ W/cm². In the present work, we have studied the $(1+1')$ -photon REMPI of HD and D₂ molecules via the $B^1\Sigma_u$ ($v=4; j=1,2$) state, considering the effects of the two above-mentioned processes. We have found that the intensity variation of the VBR and the PEAD is different for these two isotopes. This is because, in these two isotopes, the proximities of rovibrational energy levels to the resonances and the corresponding nuclear wave func-

tions are different. This difference in nuclear wave functions has been fully incorporated into our study by doing non-Franck-Condon calculations of bound-bound and bound-continuum dipole transition moments, which means that, while integrating over an internuclear separation R , the explicit dependence of the integrand (i.e., the product of the electronic dipole transition moment with the initial and the final nuclear wave functions) on R has been taken into consideration. Moreover, the explicit dependence of the bound-continuum dipole transition moments on the photoelectron energies has been taken into consideration. As a result, the dipole transition moments for these two isotopes become different for the same transitions at a particular laser intensity. Hence the strength of ionization and the higher-order coupling become different for these two isotopes. This difference in transition strengths shows up prominently in the VBR and the PEAD in the higher-laser-intensity regime, where the interference of ionization channels and the higher-order coupling become important. With the increase in laser intensity, the VBR becomes non-Franck-Condon in nature and the PEAD deviates from its shape obtained in the lower-intensity regime. We have shown here that the prominence of this effect increases with the increase in the mass of the isotopes. Moreover, we have found that the nature of the variation of the PEAD and the VBR with the laser intensity depends on the choice of different rotational levels as resonances. This feature has also been found in $(1+1')$ -photon REMPI of H₂ molecules, which supports similar experimen-

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tal observations [3] (i.e., a different VBR for different resonant rotational levels) in (3+1)-photon REMPI of H_2 molecules.

II. TRANSITION SCHEMATICS

To study $(1+1')$ -photon REMPI in HD and D_2 molecules we have chosen two transition schemes for the lower-step resonant transition: (i) the single-photon transition from the ground $X^1\Sigma_g^-(v=0, j=0)$ to $B^1\Sigma_u^-(v=4, j=1)$ levels, i.e., the $R(0)$ transition, and (ii) the single-photon transition from the ground $X^1\Sigma_g^-(v=0, j=1)$ to the $B^1\Sigma_u^-(v=4, j=2)$ level, i.e., the $R(1)$ transition. By the second photon the molecule is being excited from the resonant level to the ionization continuum, just above the $v^+=1$ level of the HD^+ and D_2^+ ions in the ground $X^2\Sigma_g^+$ state. The wavelengths are different for both the resonant and the ionizing transitions for these two isotopes. We mention here that the intensity of the laser causing the lower step transition is kept fixed at a lower value and the intensity of the laser causing the ionizing transition is varied to study the dependence of the ionization yield on the laser intensity.

We have considered vibrational levels $v=0-3$ and $5-11$ of the $B^1\Sigma_u^-$ state as the near-resonant levels. We note here that for the $R(0)$ transition scheme $j=1$ and for the $R(1)$ transition scheme both $j=0$ and 2 are allowed for the transitions via near-resonant levels. Therefore, for the $R(0)$ transition scheme, the possible values of the magnetic quantum numbers for the intermediate levels are $M_i=-1, 0,$ and 1 , but the allowed value of the magnetic quantum number is only $M_i=0$, due to the $\Delta M=0$ selection rule. Similarly, the allowed values of M_i are $-1, 0,$ and 1 for the $R(1)$ transition

scheme. To obtain the ionization rate we have summed over the contributions from ionization via intermediate levels with different values of magnetic quantum numbers.

III. THEORY

To obtain the rate of ionization in the weak-field limit, we have used the resolvent operator technique [4]. To start with we have considered the product states $|g\rangle|n\rangle, |i\rangle|n-1\rangle,$ and $|c\rangle|n-2\rangle$ as the *molecule plus photon* wave functions for the ground, intermediate (resonant and near-resonant), and continuum states, respectively. Here $|g\rangle, |i\rangle,$ and $|c\rangle$ are the bare molecular states and the $|n\rangle$'s are the photon number states. $E_g, E_i,$ and E_c are the total energies of the product states for the ground, intermediate, and continuum states, respectively. Starting from the resolvent operator equation $(Z-H)G(Z)=1$, where H is the total Hamiltonian of the system, one can write down a set of equations for the matrix elements of the resolvent operator, i.e., G_{pq} between the product states $|p\rangle$ and $|q\rangle$. By solving these equations one can derive formal expressions for the matrix elements of resolvent operators in the weak-field limit as $G_{pq}(z)=f_p/(Z-Z_0)$, where Z_0 is given as (neglecting the higher-order terms)

$$Z_0 = \sum_{M_i} [Z_{01}(M_i) + Z_{02}(M_i)], \quad (1)$$

where $Z_{01}(M_i)$ and $Z_{02}(M_i)$ are given as

$$Z_{01}(M_i) = \sum_{i=i_1, \dots, i_n} \frac{|D_{gi}|^2}{Z - E_i - s_i + \frac{i}{2} \gamma_i - \sum_{j=i_1, \dots, i_n; j \neq i} B_{ij}}$$

$$Z_{02}(M_i) = \sum_{i=i_1, \dots, i_n} \sum_{j=i_1, \dots, i_n; j \neq i} \frac{D_{gi} D_{jg} \int [D_{ic} D_{cj} / (Z - E_c)] dE_c}{\left[Z - E_i - s_i + \frac{i}{2} \gamma_i - \sum_{p=i_1, \dots, i_n; p \neq i} B_{ip} \right] \left[Z - E_j - s_j + \frac{i}{2} \gamma_j \right]},$$

with

$$B_{ij} = \frac{\left(\int [D_{ic} D_{cj} / (Z - E_c)] dE_c \right)^2}{Z - E_j - s_j + \frac{i}{2} \gamma_j}.$$

The corresponding matrix elements of the evolution operator $U_{pq}(t)$ are obtained by the inverse Laplace transform of the matrix elements of the resolvent operator $G_{pq}(Z)$, where $|U_{pq}(t)|^2$ gives the population in the state $|p\rangle$ at time t . Hence the total probability of ionization in the weak-field limit can be written as

$$P(t) = 1 - |U_{gg}(t)|^2. \quad (2)$$

Therefore the rate of ionization can be given as

$$\frac{dP}{dt} = - \frac{d}{dt} |U_{gg}(t)|^2,$$

which in the limit $t \rightarrow 0$ reduces to

$$\frac{dP}{dt} = -2 \text{Im } Z_0. \quad (3)$$

It is implicit that in the expression for $Z_{01}(M_i)$ and $Z_{02}(M_i)$ the dipole transition moments involving intermediate levels are functions of M_i , i.e., the magnetic quantum number of the intermediate levels. Here $i=i_1$ corresponds to resonant level and the others correspond to near-resonant levels. D_{pq} is the dipole transition moment between the product states $|p\rangle$ and $|q\rangle$. The ac Stark shifts and the ionization widths due to the radiation coupling of the intermediate levels $|i\rangle$ with the continuum have been denoted as s_i and γ_i , respectively. The real and imaginary parts of B_{ij} correspond to the shifting and broadening of different intermediate levels due to two-

TABLE I. Transition scheme $R(1)$.

Intensity	VBR for HD	VBR for D ₂	VBR for H ₂
1×10^8	0.1952	0.2470	
	0.8048	0.7530	
5×10^8	0.2220	0.2843	
	0.7780	0.7157	
1×10^9	0.2541	0.3359	0.1417
	0.7459	0.6641	0.8582
2×10^9	0.3222	0.4620	
	0.6778	0.5380	
3×10^9	0.3953	0.6095	
	0.6047	0.3905	
4×10^9	0.4699	0.7442	
	0.5301	0.2558	
5×10^9	0.5397	0.8222	0.2940
	0.4603	0.1778	0.7950
6×10^9	0.5979	0.8369	
	0.4021	0.1631	
7×10^9	0.6404	0.8209	
	0.3596	0.1791	

photon coupling between them via a continuum. From the expression for Z_0 it is obvious that the first term gives the sum of the contributions to the rate via the resonant and all the near-resonant channels while the second term gives the total contribution due to the interference between these ionization channels.

The total ionization rate dP/dt can be expressed as the sum of the vibrationally resolved rates, i.e., the sum of the rate of formation of molecular ions in different vibrational levels

$$\frac{dP}{dt} = \sum_{v^+} \frac{dP(v^+)}{dt}, \quad (4)$$

TABLE II. Transition scheme $R(0)$.

Intensity	VBR for HD	VBR for D ₂	VBR for H ₂
1×10^8	0.1891	0.2429	
	0.8109	0.7571	
5×10^8	0.2228	0.2901	
	0.7772	0.7099	
1×10^9	0.2661	0.3561	0.1612
	0.7339	0.6439	0.8387
2×10^9	0.3551	0.5074	
	0.6449	0.4926	
3×10^9	0.4426	0.6523	
	0.5574	0.3477	
4×10^9	0.5178	0.7218	
	0.4822	0.2782	
5×10^9	0.5672	0.6989	0.3591
	0.4328	0.3011	0.6409
6×10^9	0.5852	0.6421	
	0.4148	0.3579	
7×10^9	0.5792	0.5979	
	0.4208	0.4021	

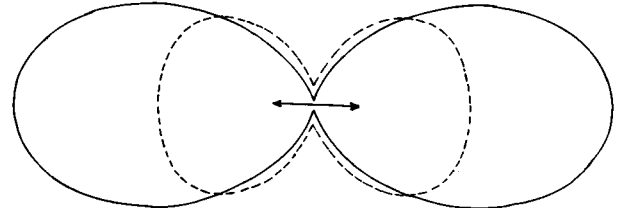


FIG. 1. Polar plot of the PEAD for REMPI of D₂ molecules considering the $R(1)$ transition scheme at a laser intensity of 5×10^9 W/cm². The figure legend is as follows: the solid line is for $v^+ = 0$ and the dashed line for $v^+ = 1$.

where v^+ is the vibrational quantum number of the molecular ion. Hence the vibrational branching ratio can be defined as

$$B(v^+) = \frac{dP(v^+)/dt}{\sum_{v^+} dP(v^+)/dt}. \quad (5)$$

Similarly the total ionization rate can be written in terms of the angle-dependent rates as

$$\frac{dP}{dt} = \int \frac{dP(\theta)}{dt} d(\cos\theta), \quad (6)$$

where θ is the photoelectron ejection angle with respect to the laser polarization axis. The angle-dependent rate can be expressed as [2,5]

$$\frac{dP(\theta)}{dt} = cI(\theta), \quad (7)$$

where

$$I(\theta) = 1 + \alpha P_2(\cos\theta) + \beta P_4(\cos\theta) + \gamma P_6(\cos\theta) + \dots$$

Here α, β, γ are the corresponding asymmetry parameters and c is a constant. All the asymmetry parameters and the constant c are functions of the laser intensity and other system parameters. The maximum order of polynomials that can contribute to $I(\theta)$ is given by $2j+2$, where j is the total angular momentum of the state being ionized.

IV. CALCULATION

In this calculation the electronic wave functions required for the calculation of electronic dipole transition moments were obtained from our previous calculations [1,2] on

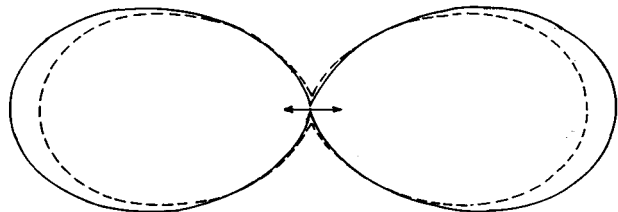


FIG. 2. Polar plot of the PEAD for REMPI of D₂ molecules considering the $R(0)$ transition scheme. Other specifications are the same as in Fig. 1.

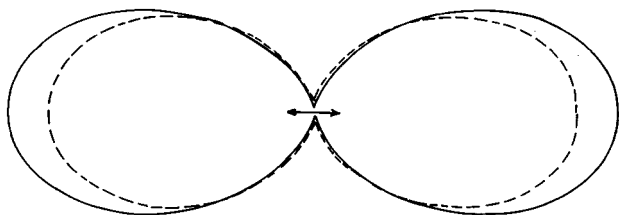


FIG. 3. Polar plot of the PEAD for REMPI of HD molecules considering the $R(1)$ transition scheme. Other specifications are the same as in Fig. 1.

REMPI of H_2 molecules. The nuclear wave functions for HD and D_2 molecules required for non-Franck-Condon calculation of dipole transition moments were obtained by using Cooley's method [6].

V. RESULTS AND DISCUSSION

We have shown here the laser intensity dependence of the (i) vibrational-branching ratio, (ii) asymmetry parameters for photoelectron angular distributions, and (iii) total and vibrationally resolved PEAD, for both $R(0)$ and $R(1)$ transition schemes in $(1+1')$ -photon REMPI of HD and D_2 molecules. By comparing these results we have also found that the nature of the dependence of the VBR and the asymmetry parameters on the laser intensity are different in these two isotopes of H_2 molecules for both transition schemes. Tables I and II give the VBR (upper line, $v^+=0$; lower line, $v^+=1$) at different laser intensities for REMPI of HD and D_2 molecules for the $R(1)$ and $R(0)$ transition schemes, respectively. For comparison we have also shown the data for H_2 molecules [1] at two laser intensities. From these two tables we find that the isotope effect is prominent on the VBR for laser intensities greater than 10^9 W/cm². The propensity for branching into the $v^+=0$ level of the isotope ions increases for heavier isotopes, which means that at a particular laser intensity the non-Franck-Condon nature of the VBR becomes more prominent for the D_2 molecules than for HD molecules. Figures 1 and 2 are the polar plots for vibrationally resolved PEAD of D_2 molecules at the laser intensity 5×10^9 W/cm² for the two transition schemes $R(1)$ and $R(0)$, respectively. A comparison of these two figures shows that the PEAD depends on the choice of resonant rotational levels in the intermediate step and for the $R(1)$ transition scheme the difference in the PEAD for $v^+=1$ and 0 is much more prominent than that for the $R(0)$ transition scheme. For the $R(1)$ transition scheme, the PEAD for the $v^+=1$ level of the D_2^+ ion is much more damped along the laser polarization

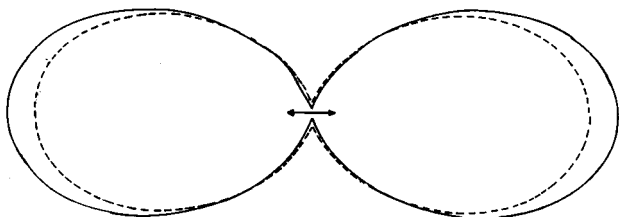


FIG. 4. Polar plot of the PEAD for REMPI of HD molecules considering the $R(0)$ transition scheme. Other specifications are the same as in Fig. 1.

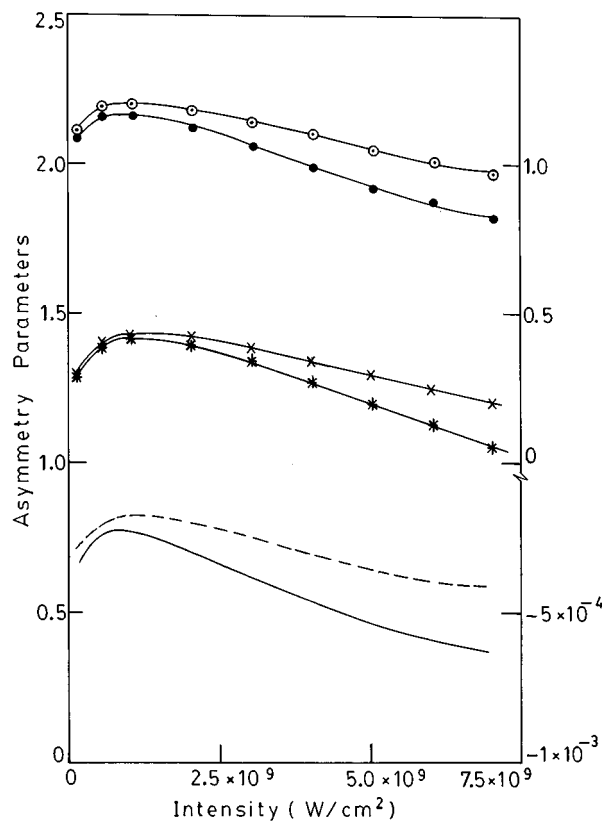


FIG. 5. Intensity variation of asymmetry parameters for the total PEAD in REMPI of HD and D_2 molecules considering the $R(1)$ transition scheme. The figure legend is as follows: $\odot\odot\odot$, α for HD molecules; $\bullet\bullet\bullet$, α for D_2 molecules; $\times\times\times$, β for HD molecules; $\star\star\star$, β for D_2 molecules; ---, γ for HD molecules; —, γ for D_2 molecules. The left ordinate scale is for α and the right ordinate scales (upper and lower) are for β and γ , respectively.

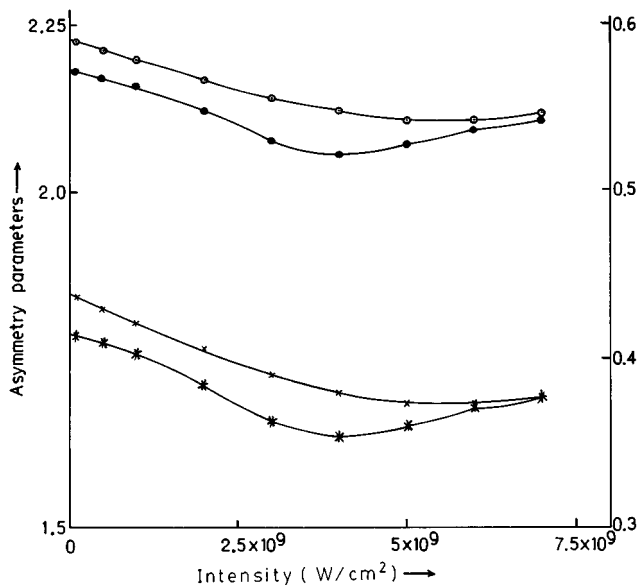


FIG. 6. Same as in Fig. 5, but the transition scheme considered here is $R(0)$. Hence the intensity variation of α and β is shown.

axis than that for the $v^+ = 0$ level. The vibrationally resolved PEAD for HD molecules at the laser intensity 5×10^9 W/cm² has been shown in Figs. 3 and 4 for the $R(1)$ and $R(0)$ transition schemes, respectively. From these four figures it is evident that the isotope effect on the PEAD is much more prominent for the $R(1)$ transition scheme than for the $R(0)$ transition scheme. Figures 5 and 6 show the intensity variation of asymmetry parameters for the total PEAD in REMPI of HD and D₂ molecules for the transition schemes $R(1)$ and $R(0)$, respectively. From these figures it is found that for both the transitions, the isotope effect on the PEAD is prominent for the laser intensity $\geq 2 \times 10^9$ W/cm². Moreover, the intensity dependence of the asymmetry parameters is different for a different choice of intermediate resonant rotational levels.

In conclusion, we have studied the isotope effect on the VBR and the PEAD in $(1+1')$ -photon REMPI of D₂ and HD

molecules at different laser intensities. We have found that the tendency for a non-Franck-Condon vibrational distribution and the degree of deviation of the total and vibrationally resolved PEAD from the usual nature (obtained in the lower-intensity regime) increases for heavier isotopes. Moreover, similar to the case of the H₂ molecule, we have found that the VBR and the PEAD for $(1+1')$ -photon REMPI of D₂ and HD molecules also depend on the choice of the resonant rotational levels in the intermediate step.

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- [1] Jainab Khatun, S. Sanyal, and Krishna Rai Dastidar, Phys. Rev. A **49**, 4765 (1994).
[2] Jainab Khatun and Krishna Rai Dastidar, Phys. Rev. A **52**, 2971 (1995), and references therein.
[3] J. W. J. Verschuur and H. B. van Linden van den Heuvell, Chem. Phys. **129**, 1 (1989).
[4] K. Rai Dastidar, Chem. Phys. Lett. **101**, 255 (1983); K. Rai Dastidar and P. Lambropoulos, Phys. Rev. A **29**, 183 (1984); L. Adhya and K. Rai Dastidar, *ibid.* **50**, 3537 (1994).
[5] Y. Itikawa, Chem. Phys. **28**, 461 (1978); S. N. Dixit and P. Lambropoulos, Phys. Rev. A **27**, 861 (1983), and references therein; S. N. Dixit and V. McKoy, J. Chem. Phys. **82**, 3546 (1985).
[6] J. W. Cooley, Math. Comput. **15**, 363 (1961).