Dissociative recombination of H_3O^+ and CH_3^+ ions at low energies

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A general first-principles theory of dissociative recombination is developed for highly-symmetric molecular ions and applied to the H_3O^+ and CH_3^+ ions, which play an important role in astrophysical, combustion, and laboratory plasma environments. The theoretical cross-sections obtained for the dissociative recombination of the two ions are in good agreement with existing experimental data from storage ring experiments.

Theory

Our study of DR in H_3^+ showed that at temperatures T>100 K the overall resonance-averaged DR rate is mainly determined by the capture of the incident electron into Rydberg states attached to the lowest excited vibrational levels of the molecular ion. In this study [Douguet12] we assume as well that the excited vibrational modes are responsible for the electron capture. We also assume that predissociation is faster than autoionization once the electron has been captured by the ion. This appears to be justified for the most of polyatomic ions [Mikhailov06,Jungen10]. With these assumptions, the DR cross-section $\sigma(E_{el})$ for capture of the electron by an ion initially on its vibrational level v' via the temporary capture into a Rydberg state associated to the vibrational ionic level v is given in [Mikhailov06]:

$$\langle \sigma(E_{el}) \rangle = \frac{2a_0\pi^2}{e^2k^2}\Gamma_v\nu^3$$

where $E_{el} = (\hbar k)^2/(2m_e)$

and Γ_v is the width of the autoionization resonance for the neutral molecule associated with the capture of the electron in the vibrational state v of the ionic core.

The DR cross-section $\sigma(E_{el})$ for electron capture into vibrational level v and electronic state Λ, with the ion initially in vibrational level v' and the electron in state Λ', can be written in terms of the scattering matrix:

$$\sigma = \frac{\pi}{k^2}|\langle v,\Lambda|\hat{S}|v',\Lambda'\rangle|^2 \quad \text{where}$$

$$\langle v,\Lambda|\hat{S}|v',\Lambda'\rangle = \int d\mathcal{Q}\langle v|\mathcal{Q}\rangle S_{\Lambda,\Lambda'}(\mathcal{Q})\langle\mathcal{Q}|v'\rangle$$

We assume that the ion is initially in the ground vibrational state $|v'\rangle = |0\rangle$. We use the normal mode approximation for the vibration (as in [Jungen08,Jungen09]) with mode coordinates labelled as $\mathcal{Q} = \{q_1, q_2, \cdots\}$, the form $\bar{S} = \exp(2\pi i\hat{\mu})$ of the scattering matrix, and an expansion of $\mu_{\Lambda,\Lambda'}(\mathcal{Q})$ in a Taylor series around the equilibrium configuration $\mathcal{Q}_0$ of the ion. This yields

$$\mu_{\Lambda,\Lambda'}(\mathcal{Q}) = \mu_{\Lambda,\Lambda'}(\mathcal{Q}_0) + \sum_i \frac{\partial\mu_{\Lambda,\Lambda'}}{\partial q_i}q_i + \dots$$

Here we use dimensionless normal modes q_1, q_2, ... , which are related to the length-unit normal coordinates S_1, S_2, ... as

$$q_i = S_i\sqrt{\mu_{red}\omega/\hbar},$$

where μ_{red} and ω are the reduced mass and the frequency of the normal mode. Retaining only zero- and first-order terms in the above expansion, the cross-section takes the form [Kokoouline11a]:

$$\sigma_i(E_{el}) = \frac{4\pi^3}{k^2}\left(\frac{\partial\mu_{\Lambda,\Lambda'}}{\partial q_i}\right)^2|\langle v_i|\hat{q}_i|0\rangle|^2$$

The index i in v_i and σ_i is used to stress that the capture occurs into the q_i vibrational mode excited by one vibrational quantum v_i. It is more convenient to use effective quantum numbers rather than quantum defects. Using the harmonic oscillator approximation to represent the vibrational states of the ionic core, the cross-section becomes:

$$\sigma_i(E_{el}) = \frac{2\pi^3}{k^2}\left(\frac{\partial\nu_{\Lambda,\Lambda'}}{\partial q_i}\right)^2\theta(\hbar\omega_i - E_{el})g\delta_{v_i,1} \quad (1)$$
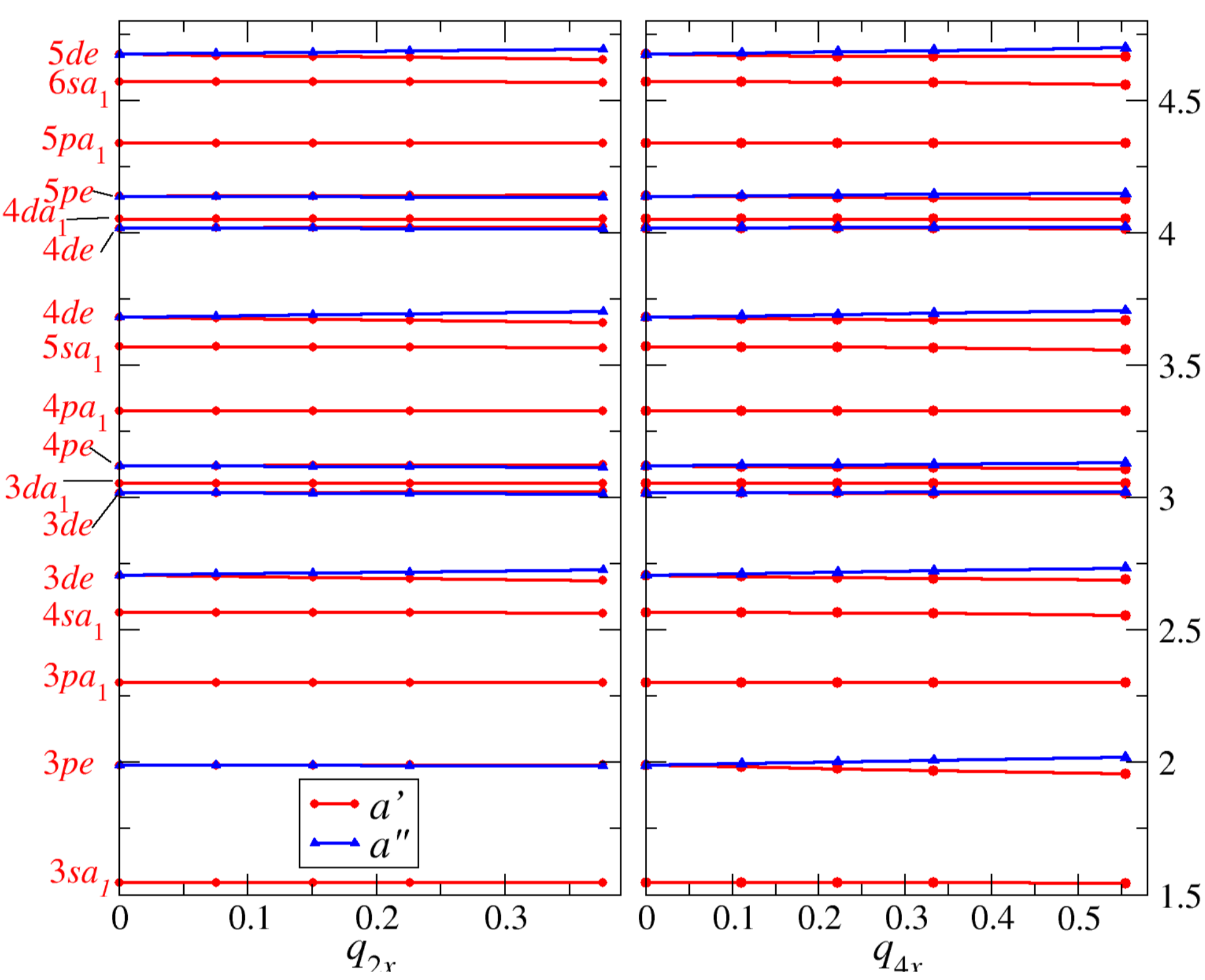
The fact that the matrix element $\langle v_i|\hat{q}_i|0\rangle$ is nonzero only for $v_i=1$ provides a rationalization for the general observation that electron capture typically occurs into the lowest vibrational level. Contributions $\sigma_i(E_{el})$ from all of the normal modes q_i must be added together to obtain the total cross-section. A particular contribution $\sigma_i(E_{el})$ should be set to 0 (at this crudest level of approximation) once the energy E_{el} of the incident electron reaches the energy of one v_i quantum.

Derivatives of the effective quantum number in Eq. (1) are obtained from ab initio calculations of potential energy surfaces (PES) of the excited Rydberg states of neutral molecules. We used Columbus code [Shepard08] adding universal Rydberg electronic orbitals optimized for Rydberg states [Kaufmann89]. The obtained PES are converted into the diagonal matrix of effective quantum number (adiabatic basis). The obtained adiabatic values ν are used to obtain coefficients (the derivatives) using the model matrix ν in the diabatic basis [Longuet-Higgins61, Staib90] of electronic states obtained for geometry $\mathcal{Q}_0$:

$$\hat{\nu}(\rho,\varphi) = \begin{pmatrix} \nu_e^{(0)} & \kappa_{ea}\rho e^{i\varphi} & \kappa_{ee}\rho e^{-i\varphi} \\ \kappa_{ea}\rho e^{-i\varphi} & \nu_a^{(0)} & \kappa_{ea}\rho e^{i\varphi} \\ \kappa_{ee}\rho e^{i\varphi} & \kappa_{ea}\rho e^{-i\varphi} & \nu_e^{(0)} \end{pmatrix} \quad (2)$$

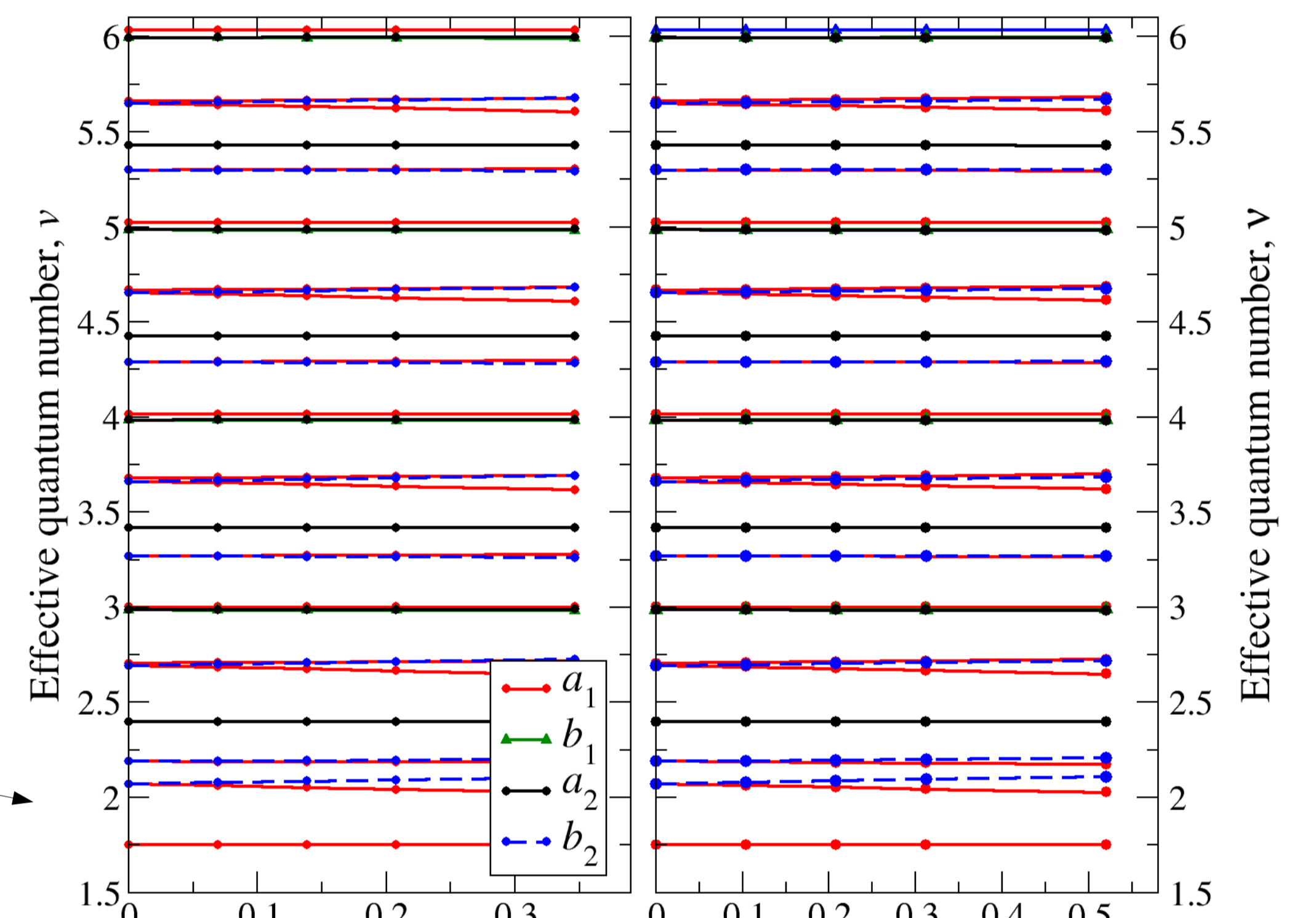Matrix (2) includes the Jahn-Teller couplings.
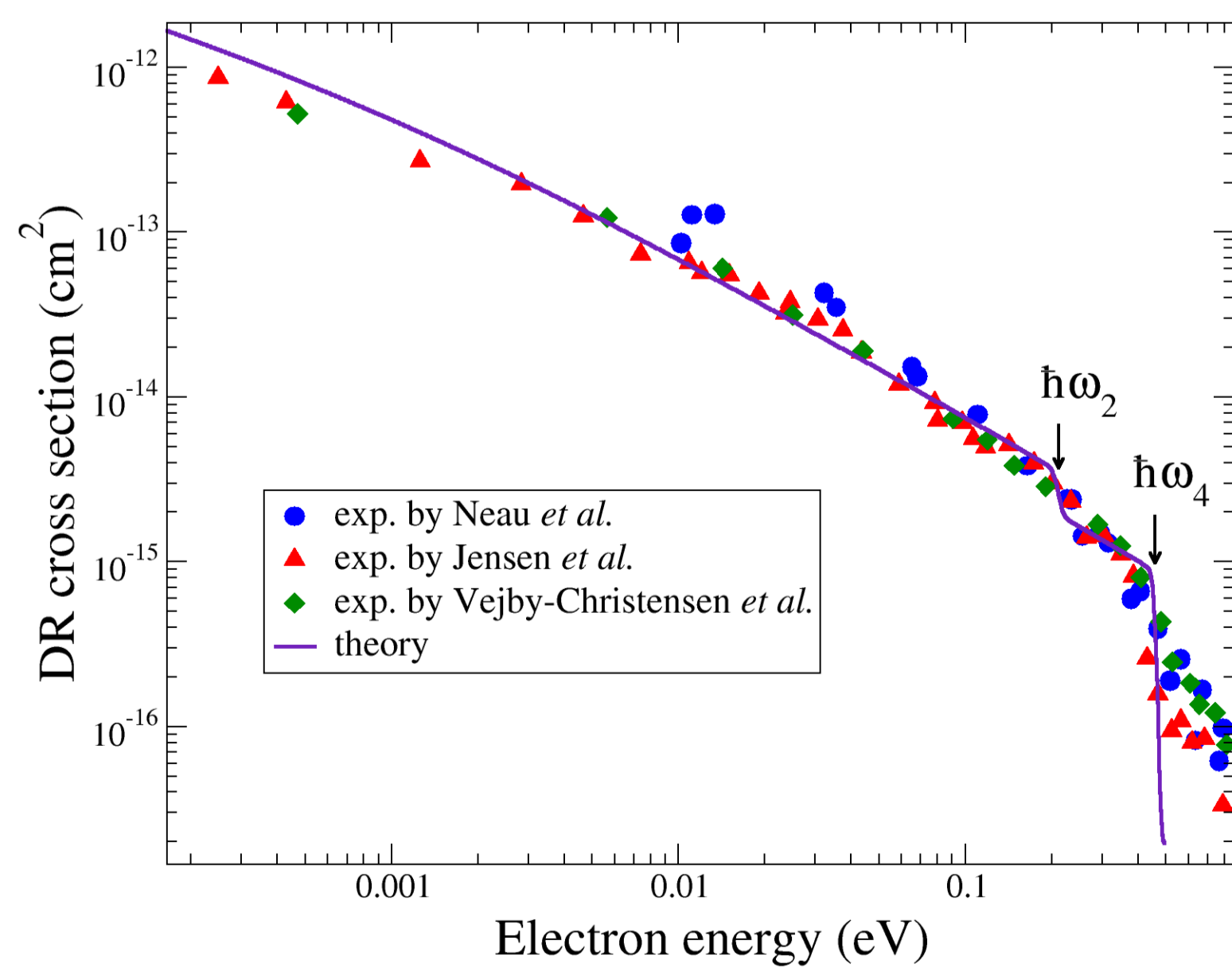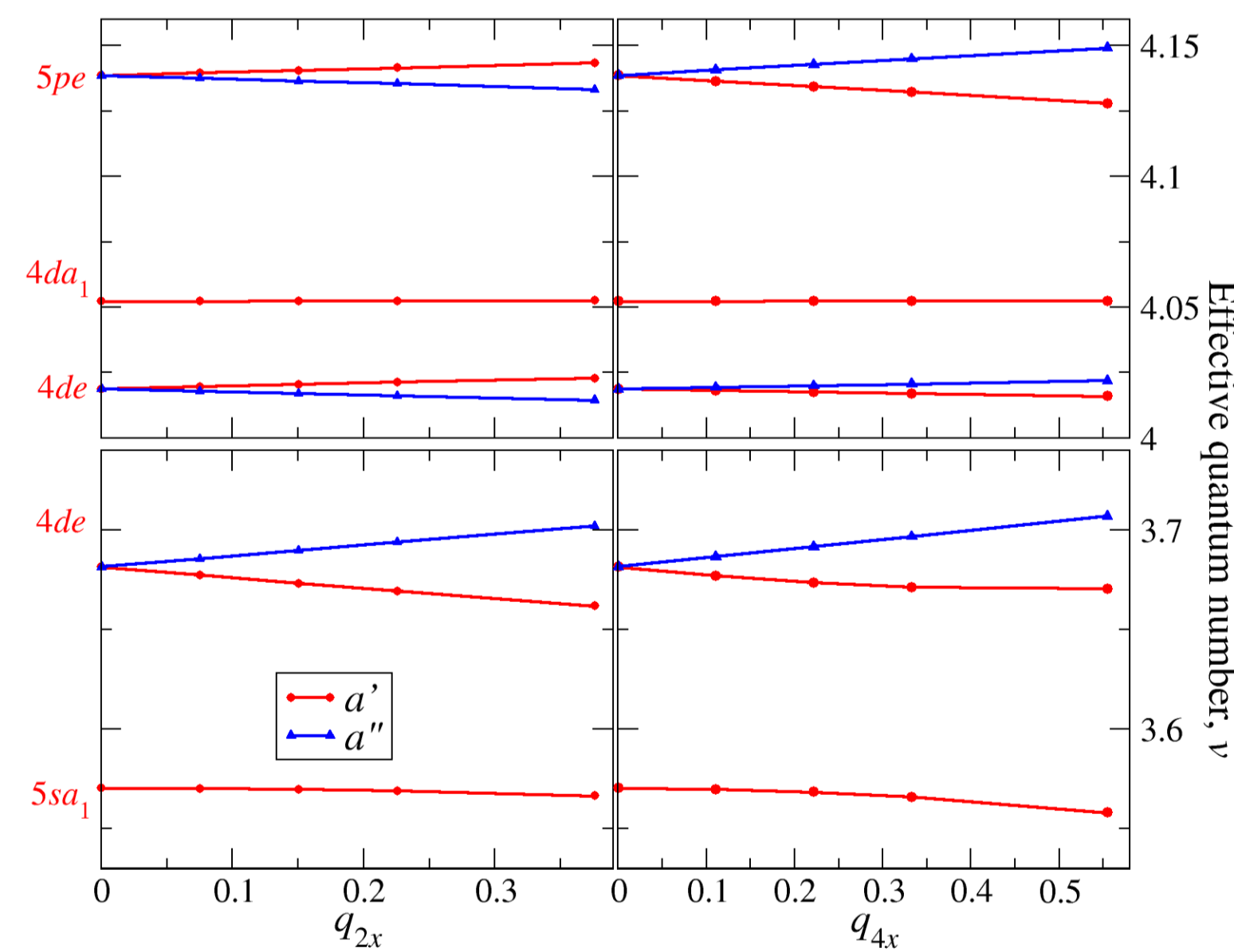
H_3O^+

CH_3^+

Effective quantum numbers $\nu(Q) = [2(E_{ion} - E_{neutral})]^{-1/2}$. The left panels in each figure show the dependence $\nu(Q)$ for several electronic states of H_3O^+ and CH_3^+ as a function of the x-component, q_{2x}, of the first doubly-degenerate vibrational modes q_2 of H_3O^+ and CH_3^+. The right panels show the same states for the second doubly-degenerate vibrational mode q_{4x}. At $q_{2x}>0$ and $q_{4x}>0$, electronic states are characterized by C_s irreducible representations for H_3O^+, i.e. a' or a'', and by C_{2v} irreducible representations for CH_3^+, i.e. a_1, a_2, b_1, or b_2.
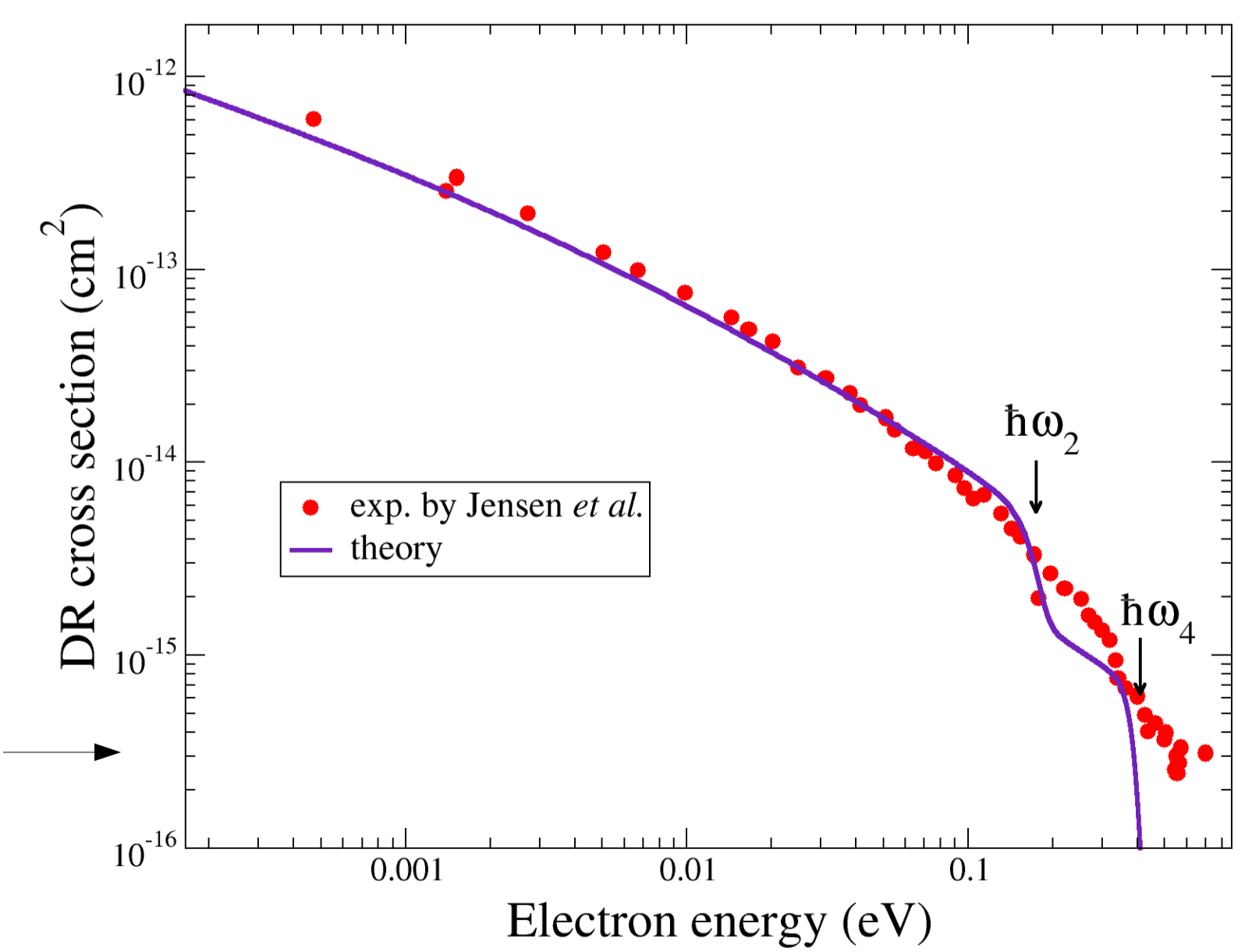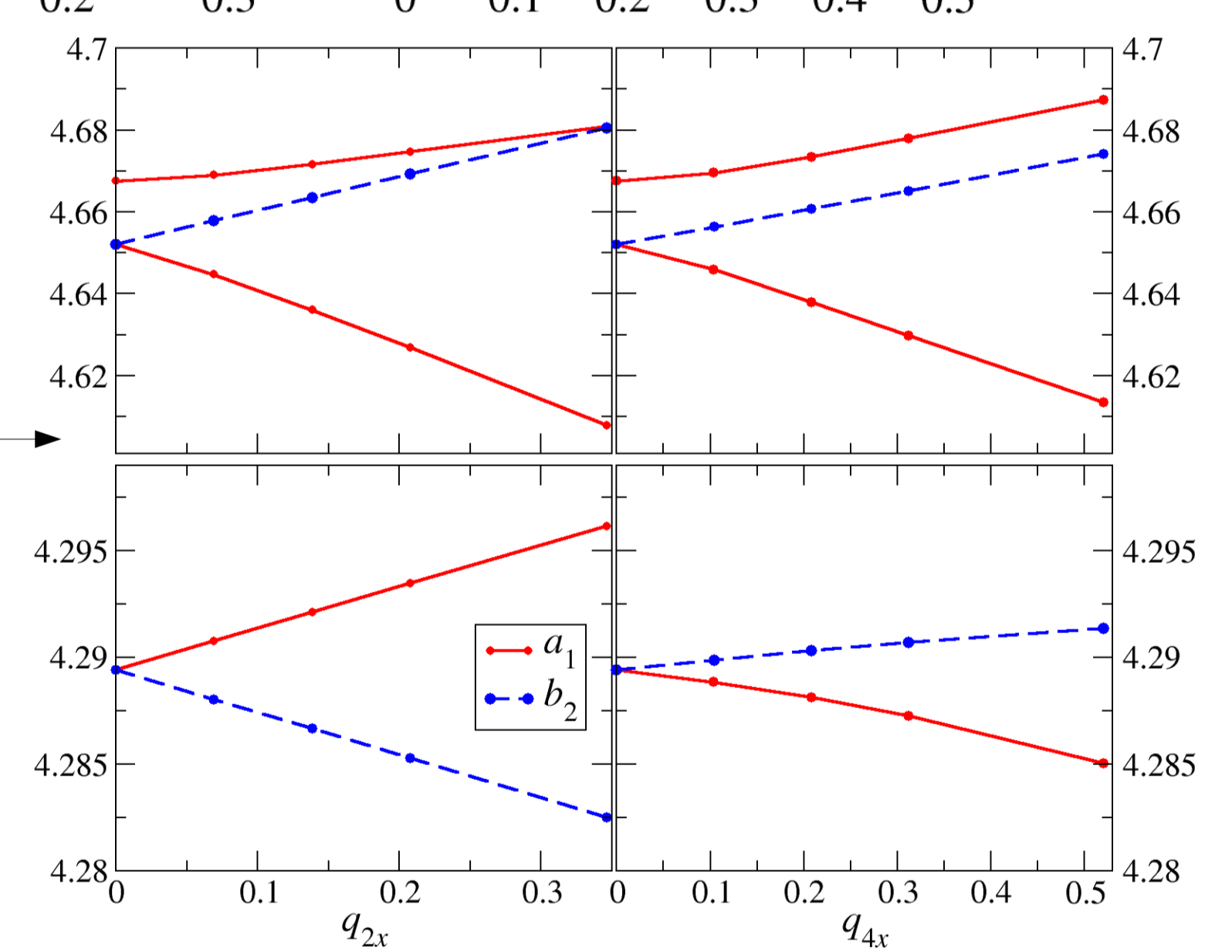
The fitted coupling parameters. Lines of numerical values correspond to the triads of electronic states included in the present treatment. The e pairs of the triads are shown here. Frequencies ω are in cm⁻¹ and calculated using the normal mode approximation and, therefore, somewhat different from the experimental values. In this study, we enumerate vibrational modes in the order of increasing energy.

	H_3O^+					CH_3^+				
	q_2 $\omega = 1705$		q_4 $\omega = 3705$			q_2 $\omega = 1448$		q_4 $\omega = 3262$		
ν_{eq}	κ_{ee}	κ_{ea}	κ_{ee}	κ_{ea}	ν_{eq}	κ_{ee}	κ_{ea}	κ_{ee}	κ_{ea}
3.681	0.056	0.029	0.046	0.047	4.65	0.083	0.062	0.041	0.045
4.018	0.012	Small	0.006	Small	4.29	0.020	Small	0.004	Small
4.139	0.013	Small	0.019	Small					

Comparison of the present theoretical and experimental DR cross-sections for H_3O^+ and CH_3^+. The plotted experimental data are from [Vejbi-Christensen97, Jensen00, Neau00] for H_3O^+ and from [Christensen97] for CH_3^+. The theoretical curves include a convolution with an experimental anisotropic distribution of electron energies with $E_{||}=0.1$ meV and $E_{\perp}=2$ meV for H_3O^+ and $E_{||}=0.5$ meV and $E_{\perp}=20$ meV for CH_3^+. The arrows indicate threshold energies for the q_2 and q_4 modes.

Conclusion

In conclusion, we stress that the present approach [Douguet12] for theoretical determination of the DR cross-section in small polyatomic closed-shell ions at energies below 1 eV is general, simple in application, and gives good agreement with experiment as well as with the detailed theoretical study made for the benchmark problem of DR in H_3^+.

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