

Inert gas atom-molecule collisions in a laser field: Vibrational excitations in homopolar molecular ions

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We investigate the effect of an electromagnetic field in the vibrational excitations of diatomic molecules, considering its collisions with noble gas atoms. Considering colinear collisions we obtain an expression for the vibrational transition amplitudes, and we apply the formalism to the specific collision $\text{He} + \text{H}_2^+$ in CO_2 laser field, in the high energy approximation. The general behavior of the multiphoton transition amplitude as a function of the relevant parameters of the system is discussed for the $0 \rightarrow 1$ vibrational excitation.

I. INTRODUCTION

The interaction of matter with electromagnetic fields (EMF) has been the subject of great interest in the last few years. Comprehension of processes involving particle scattering by atoms and atomic transitions in the presence of laser fields are very important in the study plasma heating by electromagnetic waves, resonantly excited atoms, molecular dissociation (gas breakdown), etc.¹⁻⁸ Important applications are related with the use of intense laser fields to study selective excitation of molecules and molecular dissociation by many photon processes.^{7,8}

In the present work we examine the mechanism for the vibrational excitation of diatomic molecules in the presence of a strong EMF taking into account the possibility of collisions with inert-gas atoms. The gas concentration is such that the time τ between collisions is shorter than the laser pulse, i.e., $\tau < \tau_{\text{pulse}}$. The EMF can be strong enough so that it can not be treated in a simple manner by perturbation theory.^{9,10} It is well known that the theoretical treatment of collisions involving atoms and molecules requires several approximations and usually simple models are assumed to represent the effect of the interactions.¹¹⁻¹³

The theory for the colinear collisions of an inert gas atom with a diatomic molecule is presented in Sec. II, and we apply it to homopolar molecules in Sec. III. In Sec. IV we present the numerical calculations and discussions for the specific collision process $\text{He} + \text{H}_2^+$ in the presence of a CO_2 laser field.

II. FORMULATION

For sake of simplicity, let us consider the one-dimensional collision of a diatomic molecule BC with an inert gas atom A: the colinear collision is the most favorable orientation for vibrational transition in this system.¹¹ The inert gas atom is treated as a structureless neutral particle, and its interaction with the molecule is approximated by an effective potential. The laser

field is treated as a classical plane electromagnetic wave in the dipole approximation, i.e., one considers the wavelength of the field long as compared with the size of the bound system $\text{BC} (\lambda \gg 10^{-8} \text{ cm})$, so that the vector potential $A(t) = A_0 \cos \omega t$ is spatially homogeneous. The polarization is linear and parallel to the collision direction.

We call x the deviation of the B-C bond length from equilibrium (d_0 is the equilibrium distance) and z the position of A with respect to the center of mass of the molecule BC. If r_A , r_B , and r_C are the positions of A, B, and C along the collision direction, and m_A , m_B , and m_C their masses, then

$$x = (r_B - r_C) - d_0, \quad (1)$$

$$z = r_A - \frac{m_B r_B + m_C r_C}{m_B + m_C}. \quad (2)$$

The Hamiltonian for the problem in terms of these canonical variables is

$$H = H_M + V(x, z) + (1/2\mu) [p_x - (q/c)A(t)]^2, \quad (3)$$

where

$$\mu = \frac{m_A(m_B + m_C)}{m_A + m_B + m_C}, \quad (4)$$

$$q = \frac{m_A q_M}{m_A + m_B + m_C}, \quad (5)$$

and $q_M = q_B + q_C$ is the excess charge in the molecule; q_B and q_C are the net charges of atoms B and C, and of course $q_A = 0$.

In (3), $V(x, z)$ is the effective atom-molecule interaction potential, therefore $\lim_{|z| \rightarrow \infty} V(x, z) = 0$. The specific form of $V(x, z)$ is discussed in Sec. III. The part of the Hamiltonian describing the molecular vibrations in the relative position variable x is also approximated by an effective potential $U(x)$, so that

$$H_M = (1/2m) [p_x - (q'/c)A(t)]^2 + U(x) \quad (6)$$

with

$$m = \frac{m_B m_C}{m_B + m_C} \quad (7)$$

and

$$q' = \frac{m_B q_C - m_C q_B}{m_B + m_C} \quad (8)$$

The molecule vibrational potential $U(x)$ is presented in Sec. III.

We can immediately differentiate the homopolar and heteropolar molecule cases: for an homopolar molecule $q' = 0$ and the field can not directly induce vibronic transitions in the dipole approximation, as experimentally observed,¹⁴ while an heteropolar molecule behaves as a charged oscillator in the presence of the field, interacting significantly with it. During the collision, there may exist some distortion of the molecular charge distribution causing a change in q' . This is a very small effect, and difficult to be included from first principles, therefore we neglect it here.

A possible solution for the molecular problem in the presence of an EMF is obtained by introducing a space translation transformation^{6, 15}:

$$T = \exp[-i\{\delta(t)p_x + \eta(t)\}] \quad (9)$$

where

$$\delta(t) = -\frac{q'}{mc} \int A(t') dt' = -\frac{q'A_0}{m\omega c} \sin\omega t = -\delta_0 \sin\omega t \quad (10)$$

and

$$\eta(t) = \frac{q'^2}{2mc^2} \int^t A^2(t') dt' \quad (11)$$

Under this transformation the Schrödinger equation associated with Eq. (3) is

$$\{\tilde{H}_M + (1/2\mu)[p_x - (q/c)A(t)]^2 + V[x + \delta(t), z]\} \psi(x, z, t) = i\hbar[\partial\psi(x, z, t)/\partial t] \quad (11)$$

where

$$\tilde{H}_M \phi(x, t) = \{[p_x^2/2m] + U[x + \delta(t)]\} \phi(x, t) = i\hbar[\partial\phi(x, t)/\partial t] \quad (12)$$

No exact solution can be obtained for the states $\phi(x, t)$; the so-called space translation approximation (STA) consists of neglecting completely $\delta(t)$ in Eq. (12), and therefore the bound states $\phi(x, t)$ are taken as the solution of the field free problem $\phi_n(x, t)$. This approximation is justifiable⁶ only when the characteristic range of the molecular interaction (a^{-1}) is large as compared with δ_0 , i. e., $a\delta_0 \ll 1$.

Once established the approximations for the problem, we obtain the scattering amplitude using the Green's function formalism. The approximate asymptotic solution of the Schrödinger equation

$$\tilde{H}_0 \Phi_{nk} = i\hbar \frac{\partial \Phi_{nk}}{\partial t} \quad (13)$$

obtained from (11) with $|z| \rightarrow \infty \{V[x + \delta(t), z] \rightarrow 0\}$ is

$$\Phi_{nk}(x, z, t) = \Phi_n(x, t) \xi_k(z, t) \quad (14)$$

where

$$\xi_k(z, t) = \exp\{ik[z - \alpha(t)]\} \exp(-i\epsilon_k t/\hbar) \quad (15)$$

$$\epsilon_k = (\hbar^2 k^2 / 2\mu)$$

is the analytic asymptotic solution of the z dependent part of the Hamiltonian,¹⁶ with

$$\alpha(t) = \frac{q}{\mu c} \int A(t') dt' = \frac{qA_0}{\mu\omega c} \sin\omega t \quad (16)$$

and, in the STA,

$$\phi_n(x, t) = \phi_n(x) \exp[-i(\epsilon_n/\hbar)t] \quad (17)$$

where ϕ_n is the eigenfunction and ϵ_n the corresponding eigenvalue of the field free molecular vibration Hamiltonian.

Therefore the Green's function for this problem is

$$G(x, z, t, x', z', t') = \frac{i}{2\pi} \sum_{n'} \int dk \Phi_{n',k}^*(x', z', t') \Phi_{n',k}(x, z, t) \theta(t - t') \quad (18)$$

where $\theta(t) = 1$ for $t > 0$, and vanishes for $t < 0$, and the solution of Eq. (15) is

$$\psi_{k_0, n}(x, z, t) = \phi_{k_0, n} - \int dx' dz' dt' G(x, z, t, x', z', t') \times V[x' + \delta(t'), z'] \psi_{k_0, n}(x', z', t) \quad (19)$$

Following the procedure described in the Appendix A, it is possible to write Eq. (19) in the form

$$\psi_{k_0, n}(x, z, t) = \Phi_{k_0, n}(x, z, t) + \sum_{n'} \alpha_{n', n}^\nu(A_0) \Phi_{k(\nu), n'}(x, z, t) \quad (20)$$

where

$$\alpha_{n', n}^\nu(A_0) = -\frac{i\mu\omega}{2\pi\hbar^2 k(\nu)} \int_0^{2\pi/\omega} dt \times \langle \Phi_{k(\nu), n'}(x, z, t) | V[x + \delta(t), z] | \psi_{k_0, n}(x, z, t) \rangle \quad (21)$$

In Eq. (21), the symbol $\langle \rangle$ means integration over coordinates z and x , and

$$k(\nu)^2 = k_0^2 + (2\mu/\hbar^2) (\epsilon_n - \epsilon_{n'} + \nu\hbar\omega) \quad (22)$$

The sign of $k(\nu)$ is chosen according to the asymptotic region of interest: $k(\nu)$ is positive for forward scattering ($z \rightarrow \infty$) and negative for the backward scattering case ($z \rightarrow -\infty$).

It is clear from Eqs. (19)–(22) that $\alpha_{n', n}^\nu$ represents the probability amplitude for the vibrational transition from state n to state n' due to the collision with simultaneous absorption ($\nu > 0$) or emission ($\nu < 0$) of $|\nu|$ photons.

Assuming high-energy collisions (Born approximation), we may replace $\psi_{k_0, n}$ by $\Phi_{k_0, n}$ in Eq. (21); from Appendix B we have

$$\alpha_{n', n}^\nu(A_0) = \frac{-i\mu}{(2\pi)^2 \hbar^2 k(\nu)} \tilde{V}_2[K(\nu)] \times \int_{-\infty}^{\infty} ds F_{n', n}(s) \tilde{V}_1(s) J_\nu[\alpha_0 K(\nu) + \delta_0 s] \quad (23)$$

In the application presented below, we restrict our-

selves to excitations caused by the forward scattering of the atom [$k(\nu) > 0$].

III. COLLISIONS INVOLVING HOMOPOLAR MOLECULAR ION

In this section we apply the previously described formalism to study multiphoton vibrational excitations of homopolar molecules in the presence of an EMF. As previously discussed, for homopolar molecules, $q' = 0$, and since we are considering its collision with a chargeless particle, the effect of the field appears only for homopolar molecular ions, i.e., for $q \neq 0$. Of course we can not expect the effect of the EMF to be as important as for polar molecules: here the action of the field arises only via the collision process.

For $q' = 0$ ($\delta_0 = 0$), Eq. (23) reduces to

$$a_{n',n}^{\nu}(A_0) = \frac{-i\mu}{(2\pi)^2 \hbar^2 k(\nu)} \tilde{V}_2 [K(\nu)] J_{\nu} [\alpha_0 K(\nu)] \times \int_{-\infty}^{\infty} ds F_{n',n}(s) \tilde{V}_1(s). \quad (24)$$

For homopolar molecules, the Morse potential¹⁷ is known to represent well the molecule vibrations. It is defined as:

$$U(x) = D(e^{-2ax} - 2e^{-ax}), \quad (25)$$

where D is the molecule dissociation energy and a^{-1} represents the range parameter. The eigenfunctions and eigenvalues for the Hamiltonian (6) with the Morse potential (25) and $q' = 0$ are given in Ref. 17.

It is convenient to define the ratio of the transition probability amplitude with and without the radiation field

$$R_{n',n}^{\nu} \equiv \frac{a_{n',n}^{\nu}(A_0)}{a_{n',n}^{\nu}(0)} = \frac{k(0) \tilde{V}_2 [K(\nu)]}{k(\nu) \tilde{V}_2 [K(0)]} J_{\nu} \left(\frac{qA_0 K(\nu)}{\mu\omega c} \right). \quad (26)$$

For the energy range we are considering (high energy) the dominant multiphoton processes are associated with a relatively small number of photons, and therefore $k(\nu) \cong k(0)$ [see Eq. (22)]. From (26) it is clear that $R_{n',n}^{\nu}$ is not strongly dependent on the particular choice of the interaction potential. To perform calculations we chose a model potential of the form^{11,12}

$$V_2(z) = A e^{-\beta|z|}, \quad (27)$$

so that

$$R_{n',n}^{\nu} = \frac{k(0) \beta^2 + K^2(0)}{k(\nu) \beta^2 + K^2(\nu)} J_{\nu} \left(\frac{qA_0 K(\nu)}{\mu\omega c} \right). \quad (28)$$

IV. RESULTS AND DISCUSSION

In this section we present numerical results for $R_{0,-1}^{\nu}$ considering the particular collision process between the He atom and the H_2^+ molecule ion. For this molecule the Morse potential parameters¹⁸ are $D = 2.79$ eV and $a = 0.72 a_0^{-1}$ ($a_0 =$ Bohr radius). These parameters yield $\Delta\epsilon = \epsilon_1 - \epsilon_0 = 0.28$ eV. For the EMF we chose initially typical values of a CO_2 laser, that is, field strength $\mathcal{E}_0 = 1.4 \times 10^7$ V/cm and frequency $\omega_{CO_2} = 10^3$ cm^{-1} .²⁰ The Born approximation requires the collision energy $E_0 = \hbar^2 k_0^2 / 2\mu$ to be much larger than $\Delta\epsilon$, i.e., $E_0 \gg 0.28$ eV. As we discussed previously the results are not expected to be strongly dependent on the value of the collision parameter β in Eq. (21); we assume $\beta = 10^8$ cm^{-1} which is a typical value for this parameter.¹²

To understand the relevance of multiphoton processes we investigate the dependence of $R_{0,-1}^{\nu}$ with the field strength and frequency, and with the relative collision energy.

In Table I we present the values of $R_{0,-1}^{\nu}$ for field strengths increasing from \mathcal{E}_0 to $10\mathcal{E}_0$. The colliding energy is 3 eV and $\omega = \omega_{CO_2}$. The increase in the field strength causes a significant increase in the probability amplitude for processes involving absorbed photons, and a slight decrease in the zero photon processes. The importance of multiphoton processes is clear from Table II, where the EMF frequency is decreased from ω_{CO_2} to $\omega_{CO_2}/10$, keeping $\mathcal{E}_0 = 1.4 \times 10^7$ V/cm and $E_0 = 3$ eV: for low enough frequencies, one or more photon processes become dominant over that involving no photons. In Table III the collision energy E_0 is increased up to 10 eV and the values of the field strength and frequency are those of a typical CO_2 laser. As expected, the increase in E_0 causes the multiphoton transition amplitudes to decrease.

We have also tested the sensitivity of our results with the mass m_A , which is the only parameter related to the inert gas involved in the collision. In Eq. (26),

TABLE I. Relative multiphoton transition amplitude probability $R_{0,-1}^{\nu}$ for the He- H_2^+ collision with collision energy $E_0 = 3$ eV in the presence of a CO_2 laser field ($\omega_{CO_2} = 10^3$ cm^{-1}) of variable strength ($\mathcal{E}_0 = 1.4 \times 10^7$ V/cm).

ν	$\mathcal{E}/\mathcal{E}_0$					
	1	2	4	6	8	10
0	1	1	0.99	0.99	0.98	0.96
1	0.24×10^{-1}	0.48×10^{-1}	0.97×10^{-1}	0.15	0.19	0.24
2	0.94×10^{-5}	0.38×10^{-4}	0.15×10^{-3}	0.34×10^{-3}	0.60×10^{-3}	0.94×10^{-3}
3	0.16×10^{-6}	0.13×10^{-5}	0.10×10^{-4}	0.34×10^{-4}	0.80×10^{-4}	0.16×10^{-3}

TABLE II. Relative multiphoton transition amplitude probability $R_{0 \rightarrow 1}^\nu$ for the He-H₂⁺ collision with collision energy $E_0 = 3$ eV, in the presence of a laser field of strength $\mathcal{E}_0 = 1.4 \times 10^7$ V/cm for different values of the frequency ω ($\omega_{\text{CO}_2} = 10^3$ cm⁻¹).

ν	$R_{0 \rightarrow 1}^\nu$					
	$\omega_{\text{CO}_2}/\omega$					
	1	2	4	6	8	10
0	1	0.99	0.90	0.56	0.49×10^{-1}	0.40
1	0.25×10^{-1}	0.89×10^{-1}	0.32	0.59	0.58	0.45×10^{-1}
2	0.98×10^{-5}	0.21×10^{-2}	0.42×10^{-1}	0.20	0.48	0.52
3	a	0.94×10^{-5}	0.26×10^{-2}	0.36×10^{-1}	0.19	0.46
4	a	a	0.80×10^{-4}	0.39×10^{-2}	0.44×10^{-1}	0.21
5	a	a	0.11×10^{-5}	0.25×10^{-3}	0.68×10^{-2}	0.65×10^{-1}
6	a	a	a	0.99×10^{-5}	0.71×10^{-2}	0.13×10^{-1}

^a $R_{0 \rightarrow 1}^\nu < 10^{-6}$.

since $q/\mu = q_M/(m_B + m_C)$, the only dependence in m_A comes from the various wave vectors involved in the energy balance equation. For this reason, comparing our results for the standard values of the parameters (ω_{CO_2} , \mathcal{E}_0 and $E_0 = 3$ eV) for $m_A = m_{\text{He}}$ and for $m_A \rightarrow \infty$, the values of $R_{0 \rightarrow 1}^\nu$ for ν up to 3 vary (increase) by less than a factor of 2. The general behavior of the probability amplitude for any inert gas atom is the same as described for He.

As argued previously, our results should not be very sensitive to the collision potential parameter β . For the same standard values of the parameters ω_{CO_2} , \mathcal{E}_0 and E_0 , a decrease in β by an order of magnitude causes a very slight increase in $R_{0 \rightarrow 1}^\nu$, except for $\nu = 2$, when it increases also by an order of magnitude. This is easy to understand, since the $\nu = 2$ process is the closest one to resonance, so that the transferred momentum $K(\nu)$ is minimum, and from (28), the dependence in β is enhanced.

The results presented in Tables I–III confirm the qualitative behavior one expects from simple arguments, and since the calculations are restricted to the Born approximation, the main contribution to the excitation process is due to the energy exchange between the colliding particles; energy balance is always guaranteed by the collision process.

The role of the EMF is much more significative for collisions involving polar molecules, since there exists, even in the dipole approximation, a direct contribution to the vibrational excitations from the field. Calculations for collisions of inert gases with heteropolar molecules in the present formalism are computationally more involved, and are in progress.

APPENDIX A. THE SCATTERING AMPLITUDE

In this Appendix we obtain an expression for the transition amplitude. Using Eqs. (14)–(18) in (19), this yields to

$$\begin{aligned} \psi_{k_0, n}(x, z, t) = & \Phi_{k_0, n}(x, z, t) - \frac{i}{2\pi} \sum_{n'} \phi_{n'}(x, t) \int dx' dz' dt' dk \phi_{n'}^*(x') \exp[ik(z - z')] \exp[-(i/\hbar)\epsilon_n t] \\ & \times \exp[ik\alpha_0(\sin\omega t' - \sin\omega t)] \exp[(i/\hbar)(\epsilon_n + \epsilon_{n'} - \epsilon_{k_0} - \epsilon_n)t'] \exp[(i/\hbar)(\epsilon_{k_0} + \epsilon_n)t'] V[x' + \delta(t'), z'] \psi_{k_0, n}(x', z', t'). \end{aligned} \quad (\text{A1})$$

Using the expansion of the periodic function^{1,2}

$$\exp[ik\alpha_0 \sin\omega t'] + \exp[(i/\hbar)(\epsilon_{k_0} + \epsilon_n)t'] \psi_{k_0, n}(x', z', t') \equiv \psi_{k, k_0, n}(x', z', t') = \sum_{j=-\infty}^{\infty} \psi_{k, k_0, n}^j(x', z') \exp(ij\omega t') \quad (\text{A2})$$

and

$$V[x + \delta(t), z] = \sum_{l=-\infty}^{\infty} \left[J_l \left(\frac{\delta_0}{\hbar} p_x \right) V(x, z) \right] \exp(-il\omega t), \quad (\text{A3})$$

where p_x is the momentum operator, the integration in t' yields $2i(\mu/\hbar^2) \{1/[k^2 - k^2(\nu)]\}$ where $\nu = j - l$ and $k(\nu)$ is defined by Eq. (22). Integration in k is readily performed and after taking the asymptotic limit $|z| \rightarrow \infty$ we have

$$a_{n', n}^\nu(A_0) = - \frac{\mu i}{\hbar^2 k(\nu)} \sum_{l=-\infty}^{\infty} \int dx dz \phi_{n'}^*(x) \exp[-ik(\nu)z]$$

TABLE III. Relative multiphoton transition amplitude probability $R_{0 \rightarrow 1}^\nu$, for the He-H₂⁺ collision in the presence of a CO₂ laser field ($\omega_{\text{CO}_2} = 10^3$ cm⁻¹, $\mathcal{E}_0 = 1.4 \times 10^7$ V/cm) for different values of the collision energy E_0 .

ν	E_0 (eV)				
	3	5	7	9	10
0	1	1	1	1	1
1	0.24×10^{-1}	0.16×10^{-1}	0.12×10^{-1}	0.10×10^{-1}	0.94×10^{-2}
2	0.94×10^{-5}	0.39×10^{-5}	0.22×10^{-5}	0.15×10^{-5}	0.12×10^{-5}

$$\times \{J_l[(\delta_0/\hbar)p_x] V(x, z)\} \psi_{k_0 k(\nu), n}^{\nu, t}(x, z) \quad (\text{A4})$$

From (A2) we get

$$\begin{aligned} & \psi_{k(\nu), k_0 n}(x', z') \\ &= \frac{\omega}{2\pi} \int_0^{2\pi/\omega} dt' \exp[-\omega(l+\nu)t'] \psi_{k(\nu), k_0 n}(x', z', t') \quad (\text{A5}) \end{aligned}$$

Substituting (A5) in (A4) and using (A3) we get Eq. (21).

APPENDIX B. THE BORN APPROXIMATION

In Eq. (21) we replace $\psi_{k_0, n}(x, z)$ by $\Phi_{k_0, n}(x, z)$ and get

$$\begin{aligned} a_{n', n}^{\nu}(A_0) &= -\frac{i\mu\omega}{2\pi\hbar^2 k(\nu)} \sum_{l=-\infty}^{\infty} \sum_{s=-\infty}^{\infty} J_l[\alpha_0 K(\nu)] \\ &\times \langle \phi_{n'}(x) \exp[-iK(\nu)z] \{J_s[(\delta_0/\hbar)p_x] V(x, z)\} | \phi_n(x) \rangle \\ &\times \int_0^{2\pi/\omega} \exp[i/\hbar[\epsilon_{k(\nu)} + \epsilon_{n'} - \epsilon_{k_0} - \epsilon_n + (l-s)\hbar\omega]t] dt. \quad (\text{B1}) \end{aligned}$$

After integration (B1) reduces to

$$\begin{aligned} a_{n', n}^{\nu}(A_0) &= -\frac{i\mu}{\hbar^2 k(\nu)} \sum_{s=-\infty}^{\infty} J_{s-\nu}[\alpha_0 K(\nu)] \\ &\times \langle \phi_{n'}(x) \exp[-iK(\nu)z] J_s[(\delta_0/\hbar)p_x] | V(x, z) | \phi_n(x) \rangle, \quad (\text{B2}) \end{aligned}$$

where $K(\nu) = k(\nu) - k_0$.

Using Ref. 19, we get

$$\begin{aligned} a_{n', n}^{\nu}(A_0) &= -[i\mu/\hbar^2 k(\nu)] \langle \phi_{n'}(x) \exp[-iK(\nu)z] \\ &\times \{J_{\nu}[\alpha_0 K(\nu) + (\delta_0/\hbar)p_x] V(x, z)\} | \phi_n(x) \rangle \quad (\text{B3}) \end{aligned}$$

For simplicity one usually takes $V(x, z)$ as a separable potential $V(x, z) = V_1(x) V_2(z)$ ¹² and define the Fourier transform of V_1 and V_2 by

$$V_i(y) = \int_{-\infty}^{\infty} \tilde{V}_i(q) e^{iqy} dq \quad (\text{B4})$$

and the bound state form factor by

$$F_{n', n}(q) = \int dx e^{iqx} \phi_{n'}^*(x) \phi_n(x). \quad (\text{B5})$$

Using (B4) and (B5) in Eq. (B3) we get

$$\begin{aligned} a_{n', n}^{\nu}(A_0) &= -\frac{i\mu}{(2\pi)^2 \hbar^2 k(\nu)} \tilde{V}_2[K(\nu)] \\ &\times \int_{-\infty}^{\infty} ds F_{n', n}(s) \tilde{V}_1(s) J_{\nu}[\alpha_0 K(\nu) + \delta_0 s]. \quad (\text{B6}) \end{aligned}$$

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²⁰Notice that $\delta_0 = 0.27 \times 10^{-9}$ cm for these parameters. For the Morse potential $U(x + \delta_0) = U(x) + \sum_{n=1}^{\infty} (\delta_0)^n V_n(x)$, where $V_n(x)$ are of the same order of $U(x)$. Since $\delta_0 \sim 3 \times 10^{-2}$, the STA is completely satisfactory in the present example.