

## IN SEARCH OF A NEW MOLECULE

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### ABSTRACT

**This paper presents a quantum model for collisions between Neon and Helium atoms with the formation of a HeNe quasi-molecule. The goal is to identify in this quasi-molecule the basic characteristics of a stable molecule. Using a Morse potential model, we identify modes of vibration within the  $2p_8$  and  $2p_6$  electronic potential wells created by overlapping a long-range electrostatic attractive potential with a short-range Pauli repulsive potential between  $\text{He}(1s^2)$  and  $\text{Ne}^*(2p^53p)$  atoms. The electrostatic interaction is described with a model potential which has been successfully tested in various experiments. The adiabatic molecular potentials of the HeNe system are eigenvalues of a Schrödinger equation for this model potential. For experimental testing of our results, a set of vibrational-electronic transitions between the  $2p_8$  and  $2p_6$  molecular states is suggested. Also, we predict the abundance of  $\text{Ne}^*(2p_6)$  atoms after collisions with  $\text{He}(1s^2)$  atoms *and* the absorption of infrared photons by  $\text{Ne}^*(2p_8)$  atoms.**

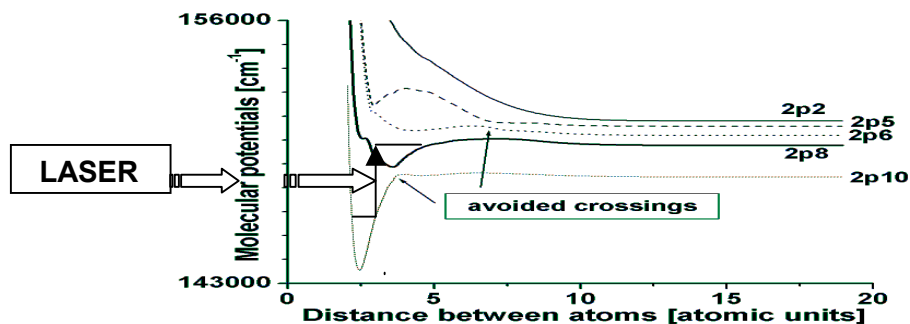
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## Motivation and goals

Two rare gas atoms in the ground state cannot form a chemical bond because the last electronic subshell of each atom is fully occupied with electrons (e.g. Helium atom has 2 electrons in the 1s subshell, Neon atom has 6 electrons on the last subshell, 2p, etc.). The Pauli principle forbids the formation of a chemical bond in this case. However, during a collision between two rare gas atoms in which at least one atom is excited, molecular interactions between atoms are identified [1, 2]. In this paper we investigate the temporary HeNe molecular structure formed during a thermal collision between a Helium-ground state and a  $\text{Ne}^*(2p^53p)$  atom at energies between 0.01 and 1 eV. The time of collision, which in this case is about  $10^{-12}$  seconds, represents the lifetime of a HeNe quasi-molecule. During this short time, the atoms interact due to electrostatic forces, the spin and the orbital motions of the electrons, and the rotation of the internuclear axis.

Previous studies (see references [1,2]) show that during a collision between a Neon atom excited on the  $2p^53p$  configuration and a Helium-ground state atom, the 3p-electron of  $\text{Ne}^*(2p^53p)$  changes its energy level within this configuration. Various electronic transitions at small internuclear distances were measured in accurate atomic crossed-beam experiments [3] and in atomic discharge cells [4,5]. A theoretical model based on the model potential for the HeNe quasi-molecule was proposed initially by Hennecart and Masnou-Seeuws [1], and later, it was improved by Bahrim *et al.* [2]. This model was successful in explaining various experiments [2-5]. Recently, the model potential from reference [2] was tested in a state-of-the-art spectroscopic experiment of disalignment of  $\text{Ne}^*(2p_2)$  and  $\text{Ne}^*(2p_7)$  atoms induced by collisions with  $\text{He}(1s^2)$  atoms performed at University of Kyoto [6].

However, to the best of our knowledge, a temporary HeNe molecule (or quasi-molecule) has never been directly observed. *This paper proposes an infrared laser spectroscopy method for the identification of vibrational modes formed within a temporary HeNe molecule as a convincing test that such a molecule forms during a He-Ne collision.*



**Figure 1:** Selected adiabatic electronic molecular states of a HeNe quasi-molecule. A transition between different states of vibration induced by absorption of a short laser pulse is suggested. The avoided crossing regions correspond to the strongest electrostatic interaction between the Ne and He atoms.

Figure 1 shows a possible transition between electronic-vibrational (molecular) states (which we plan to identify) of a HeNe quasi-molecule induced by absorption of a laser pulse. The new generation of lasers with duration of a few picoseconds or shorter could eventually modify the modes (states) of vibration of a HeNe molecular structure. This quasi-molecule has actually one period of vibration, which corresponds to the collision itself, contrary to a typical stable molecule, which has an infinite number of vibrations. This study will suggest the characteristics of the laser (i.e. the frequency) needed to identify a HeNe quasi-molecule.

This is a senior undergraduate research project in the field of atomic collisions and interactions led by the McNair Program at Lamar University. Besides its scientific value, the paper has also a pedagogic value. It is instructive for a senior undergraduate student with interest in the field of quantum mechanics and its applications to use concepts learned in advanced physics courses and discover new phenomena that revise our understanding of fundamental interactions in physics and chemistry.

The paper is organized as follows: section 2 presents the quantum model adopted to analyze a collision between two atoms. Section 3 discusses the model potential used for the interaction between He( $1s^2$ ) and Ne\*( $2p^5 3p$ ) atoms and shows a few selected adiabatic molecular states of the HeNe quasi-molecule. Section 4 presents our theoretical model for finding modes of vibration within a HeNe quasi-molecule and reports the results for the  $2p_8$  and  $2p_6$  states. Section 5 presents a set of vibrational-electronic transitions between different vibrational modes, while section 6 proposes a recipe for experimental testing of our results using a spectroscopic method. The conclusions follow in section 7.

### Dynamics of the Ne\*( $2p^5 3p$ ) + He collision

This section presents the basic model for the description of a collision between two atoms according to references [7,8]. The classical Hamiltonian for a collision between atoms of masses  $m_1$  and  $m_2$  interacting through a time-independent potential  $\mathcal{V}(\bar{R}_1 - \bar{R}_2)$  is

$$\mathcal{H}_{total}(\bar{R}_1 - \bar{R}_2) = \frac{\bar{P}_1^2}{2m_1} + \frac{\bar{P}_2^2}{2m_2} + \mathcal{V}(\bar{R}_1 - \bar{R}_2). \quad (1)$$

The vectors  $\bar{P}_1$  and  $\bar{P}_2$  represent the linear momenta of the atoms, while  $\bar{R}_1$  and  $\bar{R}_2$  are the coordinates for  $m_1$  and  $m_2$  in a laboratory fixed (LF) frame. If in equation (1) we introduce the vectors  $\bar{R}_{CM} = (m_1\bar{R}_1 + m_2\bar{R}_2)/(m_1 + m_2)$  (“the vector position of the center-of-mass (CM)”) and  $\bar{R} = \bar{R}_1 - \bar{R}_2$  (“the relative vector position” of the atoms) two other linear momenta are found: (i)  $\bar{P}_{CM} = \bar{P}_1 + \bar{P}_2$ , which represents the linear momentum of CM, and (ii)  $\bar{P} = (m_2\bar{P}_1 - m_1\bar{P}_2)/(m_1 + m_2)$ , which is the linear momentum of the reduced particle  $\mu = (m_1 m_2)/(m_1 + m_2)$ . We understand by CM a particle of mass  $M = m_1 + m_2$ . Thus, in equation (1) the kinetic terms are

$$\frac{\bar{P}_1^2}{2m_1} + \frac{\bar{P}_2^2}{2m_2} = \frac{\bar{P}_{CM}^2}{2M} + \frac{\bar{P}^2}{2\mu}. \quad (2)$$

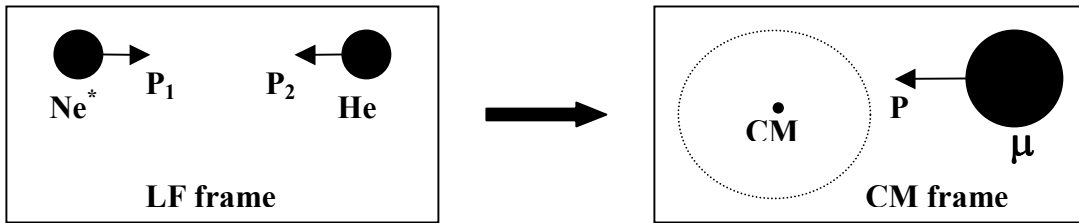
and consequently, the total classical Hamiltonian (1) becomes

$$\mathcal{H}_{total}(\bar{R}, \bar{R}_{CM}) = \frac{\bar{P}_{CM}^2}{2M} + \frac{\bar{P}^2}{2\mu} + \mathcal{V}(\bar{R}, \bar{R}_{CM}). \quad (3)$$

If we choose a coordinate system with the origin in CM, then the term  $\frac{\bar{P}_{CM}^2}{2M}$  disappears from equation (3) and  $\mathcal{H}_{total}(\bar{R}, \bar{R}_{CM})$  becomes

$$\mathcal{H}_{total}(\bar{R}) = \frac{\bar{P}^2}{2\mu} + \mathcal{V}(\bar{R}). \quad (4)$$

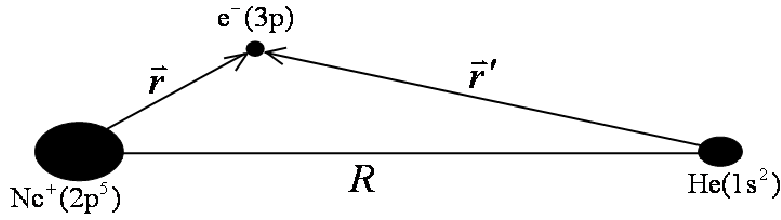
Here,  $\bar{P}$  is the total linear momentum of the particle  $\mu$  with respect to CM. The transformation from the LF frame to the CM frame is shown in figure 2. The central potential  $\mathcal{V}(\bar{R})$  which describes the electronic interaction between atoms is discussed in section 3 for the particular case of the He( $1s^2$ )-Ne\*( $2p^53p$ ) system.



**Figure 2:** The transformation from the LF frame to the CM frame. The range of the central potential  $\mathcal{V}(\bar{R})$  from equation (4) is suggested by a dashed circle.

### A model potential for the He( $1s^2$ )-Ne\*( $2p^53p$ ) interaction

A complete description of the interaction between Helium and Neon atoms requires a Hamiltonian that includes both the electrostatic interaction and the relativistic interaction due to the orbital and spin motions of the electrons. We adopt the model potential from references [1,2] indicated in figure 3, in which a complex multi-body interaction between Ne\*( $2p^53p$ ) atom with the He-ground state atom is simplified into *three* two-body Coulomb interactions: (i)  $e^-(3p) + Ne^+(2p^5)$  (for an isolated Ne atom, described by the atomic Hamiltonian,  $H(\bar{r})$ ), (ii)  $e^-(3p) + He$  atom (described by a potential  $V_{int}(R)$ ), and (iii) the core-core interaction (described by a potential  $W_{CC}(R)$ ).



**Figure 3:** A model potential for the interaction between  $\text{Ne}^*(2p^5 3p)$  and  $\text{He}(1s^2)$  atoms.

The total electronic Hamiltonian of the He-Ne system is

$$H(R, \bar{r}) = H(\bar{r}) + V_{\text{int}}(R) + W_{\text{CC}}(R). \quad (5)$$

For thermal collisions as those studied in references [2-6] the spin-orbit interaction should be included in  $H(R, \bar{r})$ . But only the  $\text{Ne}^*(2p^5 3p)$  atom contributes to the electronic angular momentum  $\bar{J} = \bar{L} + \bar{S}$  of the HeNe system because  $\text{He}(1s^2)$  has  $\bar{J} = 0$ . The operators  $\bar{J}^2$  and its projection,  $J_z$ , along the internuclear axis  $\bar{R}$  commute with the Coulomb part of  $H(R, \bar{r})$ .

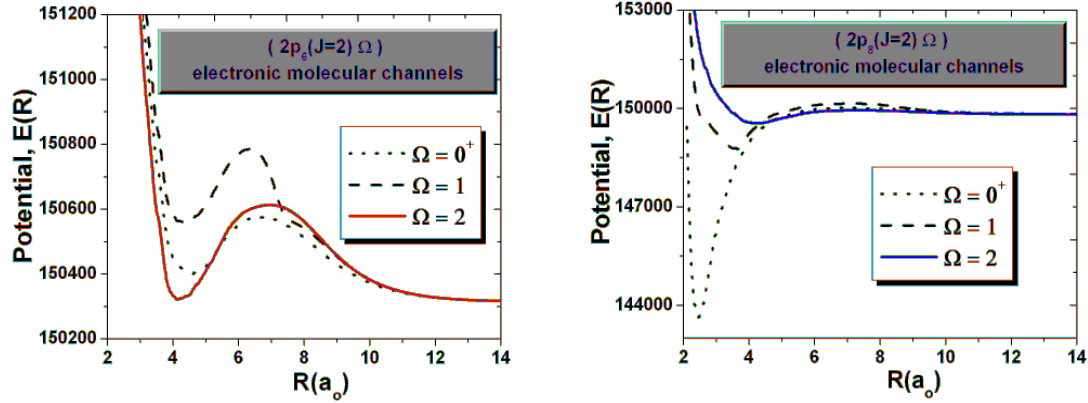
Also, for thermal collisions the electrons follow adiabatically the motion of the nuclei. Therefore, the electronic motion can be treated separately, and the Born-Oppenheimer approximation [8] can be used. Because the interaction  $\mathcal{V}(\bar{R})$  in equation (4) is time-independent, the electronic potentials (labeled by  $E(R)$ ) of the  $\text{Ne}^*(2p^5 3p)$ -He quasi-molecule are solutions of a time-independent Schrödinger equation

$$H(R, \bar{r})\psi(R, \bar{r}) = E(R)\psi(R, \bar{r}), \quad (6)$$

in an adiabatic basis set of functions,  $\psi(R)$ . Because the operators  $\bar{J}^2$  and  $J_z$  commute with  $H(R, \bar{r})$ , the electronic molecular states will be characterized by three quantum numbers: the electronic angular quantum number  $J$ , the quantum number  $\Omega$  associated to the projection of the electronic angular momentum on the internuclear axis, and the parity<sup>1</sup> quantum number,  $\pi$  (which can be either +1 or -1). Therefore, the electronic molecular states will be labeled by  $(2p_i(J)\Omega^\pi)$ . Figure 4 shows the adiabatic molecular potentials  $E(R)$  that converge asymptotically toward the  $2p_6(J=2)$  and  $2p_8(J=2)$  atomic states of the  $\text{Ne}^*(2p^5 3p)$  configuration, which are of interest for the present study. During the interaction between He and Ne atoms, each atomic state is transformed into three molecular channels with  $\Omega = 0^+, 1$  and  $2$ . The  $\text{Ne}^*(2p^5 3p)$ -He quasi-molecule has a total of 36 adiabatic electronic molecular states, which will be reported elsewhere. Figure 4 shows that all molecular states  $(2p_6(J=2)\Omega)$  and  $(2p_8(J=2)\Omega)$  have a bonding character at small  $R$ . Bonding states are characteristics for stable molecules, only. This interesting result has encouraged us to try finding vibrational states in these potential wells, because a

<sup>1</sup> The parity corresponds to a geometric operation called “inversion with respect to CM” applied to molecular states.  $\pi$  is given by  $(-1)^J$ , for  $\Omega = 0^+$  states. The  $\Omega \neq 0$  states are degenerate with respect to  $\pi$  (which means they have the same energy for both  $\pi = +1$  and  $-1$  states).

mode of vibration is the clear signature for the formation of a molecule. To achieve this goal we develop the model discussed in the next section.



**Figure 4:** Electronic (adiabatic) molecular potentials which asymptotically converge toward the  $\text{Ne}^*(2p_6)$  and  $\text{Ne}^*(2p_8)$  atomic states of the  $2p^53p$  configuration.

### Theoretical model

This section presents the quantum model we have developed for the identification of vibrational modes in a  $\text{He-Ne}^*(2p^53p)$  quasi-molecule. We start by fitting the bottom region of each potential well with a simple parabolic function

$$U(x) = \frac{1}{2} kx^2 \quad (7)$$

where  $k$  represents the elastic constant for a harmonic oscillatory motion, symmetric with respect to an origin  $x = 0$ . The value for  $k$  is specific for each potential well. The oscillatory motion within a potential well is actually done about an equilibrium position,  $R_0$ . If we let  $R_0$  be the internuclear distance at the bottom of the well, and let  $E_{\min}$  be the potential at distance  $R_0$ , then in the parabolic approximation  $U = \frac{1}{2} kx^2$ , the terms  $U$  and  $x$  mean:  $U = E - E_{\min}$  and  $x = R - R_0$ . According to reference [9], we can describe a parabolic oscillatory motion with the following Schrödinger equation:

$$-\frac{\hbar^2}{2\mu} \frac{d^2 \psi_N(x)}{dx^2} + \frac{1}{2} kx^2 \psi_N(x) = E_N \psi_N(x), \quad (8)$$

where  $\hbar = h/2\pi$  is Planck's constant. The general solution to equation (8), which is actually the eigenfunction for a parabolic potential  $U(x)$ , is

$$\psi_N(x) = a_N H_N(\gamma x) \exp(-(\gamma x)^2/2), \quad (9)$$

where  $a_N = \left( \frac{\gamma}{\sqrt{\pi} 2^N N!} \right)^{\frac{1}{2}}$  is a constant,  $H_N(\gamma x) = (-1)^N \exp((\gamma x)^2) \frac{d^N}{dz^N} \exp(-(\gamma x)^2)$  are *Hermite's Polynomials* [10], and  $N$  is a non-negative integer (0, 1, 2, ...) called the *vibrational quantum number*. The factor  $\gamma$  is defined as  $\gamma = (k\mu)^{\frac{1}{4}}/\hbar^{\frac{1}{2}}$ . The eigenvalues,  $E_N$ , in equation (8) represent the vibrational energy levels for a parabolic potential  $U(x)$ . With respect to  $E_{\min}$ , these energies are

$$E_N - E_{\min} = \hbar\omega_0 (N + \frac{1}{2}), \quad (10)$$

where  $\omega_0 = \sqrt{k/\mu}$  is the angular frequency of a harmonic oscillator. From equation (10), the energy difference between consecutive vibrational levels is

$$E_{N+1} - E_N = \hbar\omega_0, \quad (11)$$

where  $\hbar\omega_0$  is called the “vibrational photon”. Using equation (11), for each molecular state,  $E(R)$  (given by equation (6)), we can build up an energy diagram associated to a HeNe molecule that has a *harmonic oscillation for the nuclear motion*.

However, a perfectly symmetric oscillatory motion is an ideal case. In reality, for any molecule there is an additional anharmonic effect due to a centrifugal distortion toward large internuclear distances that is caused by the rotational motion of the internuclear axis. As a result, the vibrational states of any molecule are not equally spaced as indicated by equation (11), and therefore, a more accurate model is necessary. A model that better describes the electronic molecular potentials uses a Morse potential,

$$V(R) = D_e [e^{-2\alpha(R-R_0)} - 2e^{-\alpha(R-R_0)}] . \quad (12)$$

In equation (12),  $D_e$  is the dissociation energy of the potential well, and  $\alpha$  is an adjustable parameter. The Morse potential model gives a potential well that is steeper at small internuclear distances than the parabolic potential. At large internuclear distances, a Morse potential better reproduces the Coulomb attraction between electrons and nuclei. If we expand  $V(R)$  into a Taylor series relative to the variable  $R - R_0$ , we get

$$V(R) = D_e [-1 + \alpha^2 (R - R_0)^2 + \dots] . \quad (13)$$

In the first order approximation, we identify the function  $V(R) + D_e = D_e \alpha^2 (R - R_0)^2$ . If we compare this function with the parabolic function,  $U = \frac{1}{2}k(R - R_0)^2$ , we get

$$D_e \alpha^2 = \frac{1}{2}k . \quad (14)$$

Solving the Schrödinger equation

$$-\frac{\hbar^2}{2\mu} \frac{d^2 \psi_N(R)}{dx^2} + V(R) \psi_N(R) = E_N \psi_N(R) \quad (15)$$

leads to a series of vibrational states for the Morse potential (12),

$$E_N - E_{\min} = \hbar\omega_0 \left[ \left( N + \frac{1}{2} \right) - \beta \left( N + \frac{1}{2} \right)^2 \right], \quad (16)$$

where  $\beta$  is a constant of *anharmonicity* and is given in reference [8]

$$\beta = \hbar\omega_0 / 4D_e. \quad (17)$$

Equation (16) is written with respect to  $E_{\min}$ . Compared with the eigenvalues given in equation (11) for a parabolic potential, the equation (16) includes the contribution of the anharmonic oscillatory motion of nuclei. Also, the wavefunctions given in equation (9) for a simple harmonic potential should now be modified in order to include the anharmonic correction. Hereafter, each vibrational molecular state will be labeled by  $(2p_i(J)\Omega^\pi N)$  because in addition to the quantum numbers for the electronic motion ( $J$ ,  $\Omega$  and  $\pi$ ), we have to introduce a new quantum number,  $N$ , for the vibrational motion of nuclei.

### Procedure to calculate the modes of vibration

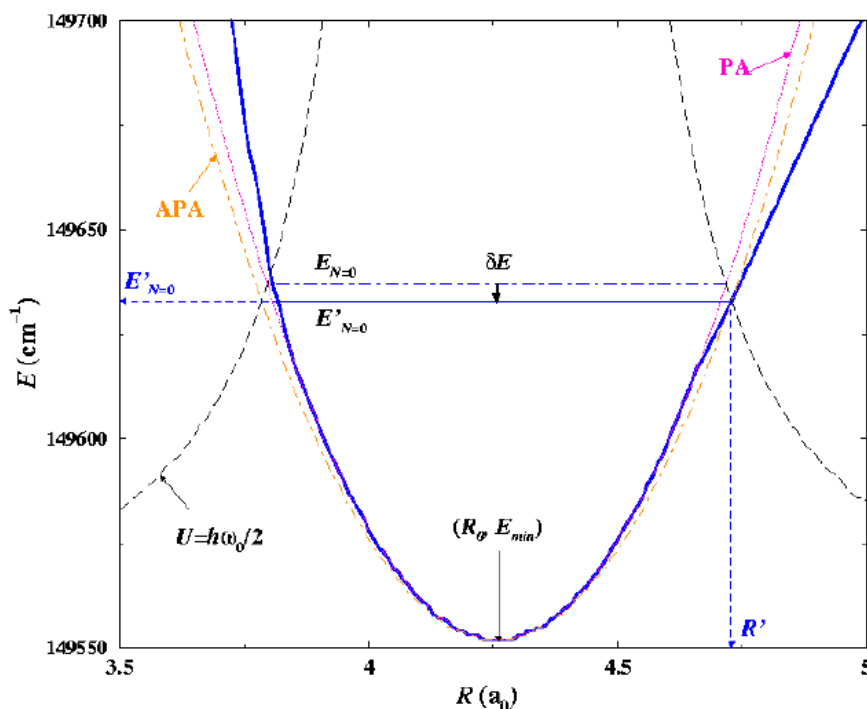
In the following, we present the procedure developed to find vibrational states. Our model uses a best fitting procedure of the electronic potential wells  $E(R)$  (shown in figure 5) with an adjusted parabolic function (7) in the first order and a Morse potential (12) in the second order.

- (1) First, we look for a parabolic approximation (**PA**) that best fits the potential well of a  $(2p_i(J)\Omega^\pi)$  electronic molecular state near  $R_0$ .
- (2) Next, we calculate the elastic constant  $k = 2(E - E_{\min}) / (R - R_0)^2$  and the angular frequency  $\omega_0 = \sqrt{k/\mu}$  for a harmonic oscillatory motion, which leads to the energy of the vibrational photon,  $\hbar\omega_0 = E_N - E_{N-1}$ , associated to a  $(2p_i(J)\Omega^\pi)$  state.
- (3) We calculate the vibrational ground state  $E_{N=0} = \frac{1}{2}\hbar\omega_0 + E_{\min}$  of the  $(2p_i(J)\Omega^\pi)$  state. If  $E_{N=0} - E_{\min}$  is larger than the width of the region where a parabolic function fits a  $(2p_i(J)\Omega^\pi)$  state then an adjusted parabolic approximation (**APA**) is applied to get  $E'_{N=0}$  and  $R'$  so that  $U = \frac{1}{2}k(R' - R_0)^2$  is set to  $E'_{N=0} - E_{\min} = \frac{1}{2}\hbar\omega_p$ .



This adjustment shifts the vibrational ground state downward by  $\delta E = E_{N=0} - E'_{N=0}$ , as indicated in figure 5 for the test case  $(2p_8(J=2)\Omega=2)$ . For upper vibrational states, with  $N = 1, 2, 3, \dots$ , the energy shift  $\delta E$  should be multiplied by  $(2N + 1)$ :

$$\delta_N = (2N + 1)\delta E. \quad (18)$$



**Figure 5:** The vibrational ground state of the  $(2p_8(J=2)\Omega=2)$  electronic molecular potential. The parabolic and adjusted parabolic approximations are indicated.

- (4) We read the dissociation energy,  $D_e$ , from equation (13), for a Morse potential that best fits the potential well and calculate the parameter  $\alpha_p = \sqrt{k/2D_e}$ . The value for  $D_e$  and  $\alpha_p$  are adjusted until the Morse potential best fits a broader region of the potential well. We label the adjusted parameter by  $\alpha_M$ .
- (5) Next, we calculate a new elastic constant,  $k_M = 2D_e\alpha_M^2$ , and the energy of the vibrational photon  $\hbar\omega_M = \hbar\sqrt{k_M/\mu}$  for a Morse potential. The anharmonicity factor from equation (17) can now be calculated using formula:  $\beta = \hbar\omega_M/4D_e$ .
- (6) Finally, we calculate the vibrational states  $E_N^M$  according to equation (16).

Table 1 gives the relevant parameters discussed above for the vibrational ground state of  $(2p_6(J=2)\Omega=2)$  and  $(2p_8(J=2)\Omega=2)$  molecular channels. On the first two lines we give the parameters that lead to  $E_{N=0}^P$  in the parabolic approximation, while on the last two lines we give the parameters used for  $E_{N=0}^M$  in the Morse model. For the  $2p_6$  state a parabolic approximation is applied (therefore, there is no energy shift  $\delta E$ ), while for the  $2p_8$  state an adjusted parabolic approximation is required, as shown in figure 5.

**Table 1:** The relevant parameters for the vibrational ground state ( $N=0$ ) of the  $(2p_6(J=2)\Omega=2)$  and  $(2p_8(J=2)\Omega=2)$  molecular channels. The percentage shift  $\Gamma$  from equation (19) is indicated.

State	$R_0(\text{a}_0)$	$E_{\min}(\text{cm}^{-1})$	$k$	$k_P(\text{APA})$	$\omega_P$ ( $10^{13}\text{rad/s}$ )	$E_{N=0}^P$ ( $\text{cm}^{-1}$ )	$\delta E$ ( $\text{cm}^{-1}$ )
$2p_6$	4.233	150319	350	---	2.12	150375.16	0
$2p_8$	4.257	149552	800	727.162	3.05	149632.95	4.0
State	$\alpha_P$	$D_e(\text{cm}^{-1})$	$\alpha_M$	$k_M$	$\beta$	$E_{N=0}^M$ ( $\text{cm}^{-1}$ )	$\Gamma(\%)$
$2p_6$	0.507	681	0.60	490.32	0.0488	150383.85	15.5
$2p_8$	0.816	546	0.85	788.97	0.0772	149633.22	0.3

The percentage shift in energy between the ground states calculated with a Morse potential,  $E_{N=0}^M$ , and calculated with a simple parabolic approximation,  $E_{N=0}^P$ , is defined as

$$\Gamma(\%) = \left( \left| E_{N=0}^M - E_{N=0}^P \right| / \left( E_{N=0}^P - E_{\min} \right) \right) \cdot 100\%. \quad (19)$$

This percentage shift is indicative for the precision attained in our calculations and is given in table 1 for both  $(2p_6(J=2)\Omega=2)$  and  $(2p_8(J=2)\Omega=2)$  molecular channels. Values of 0.3% and 15.5% respectively, are small enough to make us confident regarding the procedure described above for the calculation of the energy diagram for the vibrational motion within a  $2p_i(J)\Omega^\pi$  molecular channel.

### Results for the $(2p_6(J=2)\Omega=2)$ and $(2p_8(J=2)\Omega=2)$ states

Table 2 gives the vibrational energy levels for the  $(2p_6(J=2)\Omega=2)$  and  $(2p_8(J=2)\Omega=2)$  molecular channels. Figure 6 shows the energy diagram and the wave functions (9) for the nuclear motion within a HeNe quasi-molecule, corrected by the anharmonicity factor (17). A wave function associated to the nuclear motion allows “to visualize” the nuclei during a collision as quantum particles. Quantum physics considers

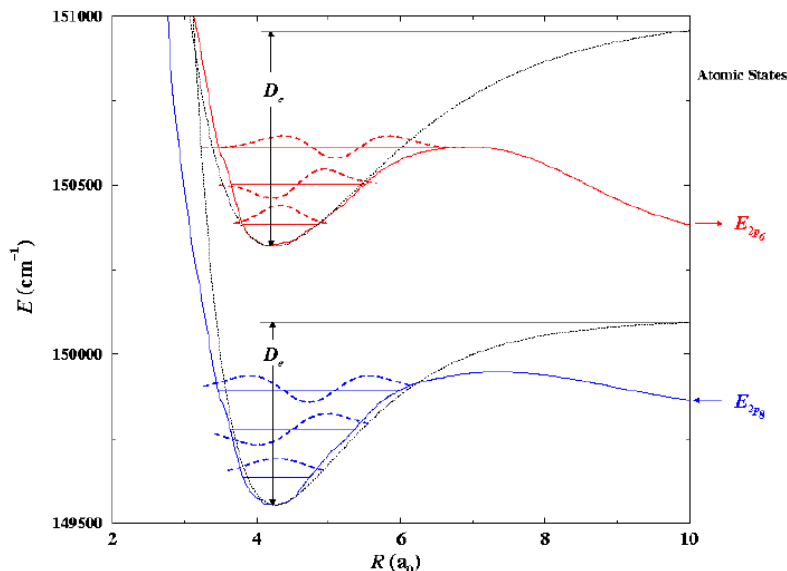
that any particle in motion has a wave behavior. Also, for each vibrational energy level in table 2 we give the absolute uncertainty,  $\Delta_N$ , defined as

$$\Delta_N = \delta_N + |E_N^M - E_N^P|, \quad (20)$$

where  $\delta_N$  was introduced by equation (18). The quantity  $(E_N^M - E_N^P)$  represents the energy difference between the vibrational energy levels calculated with the (adjusted) parabolic approximation and the Morse potential model, respectively.

**Table 2:** The vibrational energies,  $E_N$ , calculated with a Morse potential model, for two molecular states, the atomic energies  $E_{2p_i}$ , the energy splitting  $\Delta E_{N,N-1}$  between adjacent vibrational states, the localization of a vibrational state (which is between  $R_{\min}$  and  $R_{\max}$ ), and the absolute uncertainty,  $\Delta_N$ , for each energy  $E_N$  are given.

$(2p_i(J)\Omega^\pi)$ molecular states	$E_{2p_i}$ ( $\text{cm}^{-1}$ )	$N$	$E_N$ ( $\text{cm}^{-1}$ )	$\Delta E_{N,N-1}$ ( $\text{cm}^{-1}$ )	$R_{\min}$ ( $a_0$ )	$R_{\max}$ ( $a_0$ )	$\Delta_N$ ( $\text{cm}^{-1}$ )
$2p_6(J=2)2^\pm$	150317	0	150384	----	3.81	4.85	8.7
		1	150504	120	3.65	5.51	16.3
		2	150611	107	3.48	6.72	11.0
$2p_8(J=2)2^\pm$	149826	0	149635	----	3.81	4.74	4.2
		1	149778	143	3.64	5.36	30.6
		2	149894	116	3.46	6.00	---



**Figure 6:** The energy diagram for the  $(2p_6(J=2)\Omega=2)$  (in red) and  $(2p_8(J=2)\Omega=2)$  (in blue) molecular states of a  $\text{HeNe}^*$  quasi-molecule. The wave functions for the nuclear motion (dashed lines), the Morse potentials (dotted dark lines) and  $D_e$  from equation (12) are indicated.

Compared with a parabolic approximation, which gives vibrational energies evenly spaced (i.e.  $E_N^P - E_{N-1}^P = 112 \text{ cm}^{-1}$  and  $162 \text{ cm}^{-1}$  for the  $2p_6$  and  $2p_8$  molecular channels, respectively), the Morse potential model takes care of the anharmonic effect correctly, as shown in table 2, where we see that the energy splitting  $\Delta E_{N,N-1} = E_N^M - E_{N-1}^M$  decreases for higher vibrational states.

### Transitions between vibrational-electronic molecular states

An upward vibrational-electronic transition takes place when a photon of energy  $h\nu = |E_{N'} - E_N|$  (where  $\nu$  is the frequency of the photon) equal to the energy difference between two  $(2p_i(J)\Omega^\pi N)$  levels is absorbed. The transition is “allowed” if it obeys simultaneously the following four selection rules: (i) it should be vertical at a well-defined  $R$  (known as “the Franck-Condon principle” [8]), (ii) for nuclear motion  $\Delta N = \pm 1$  [11], (iii) for electronic motion  $\Delta J = 0, \pm 1$  [8] and  $\Delta \Omega = 0, \pm 1$  [11], and (iv) for parity  $\Delta \pi = \pm 1$  [8].

Table 3 gives the characteristics of the transitions between vibrational levels of the  $(2p_6(J=2)\Omega=2)$  and  $(2p_8(J=2)\Omega=2)$  electronic states presented in figure 7. The energy,  $h\nu$ , the wavelength  $\lambda$ , the frequency,  $\nu$ , and the period,  $T = 1/\nu$ , of a “transition photon” that induces excitation between vibrational-electronic states are given. In table 3,

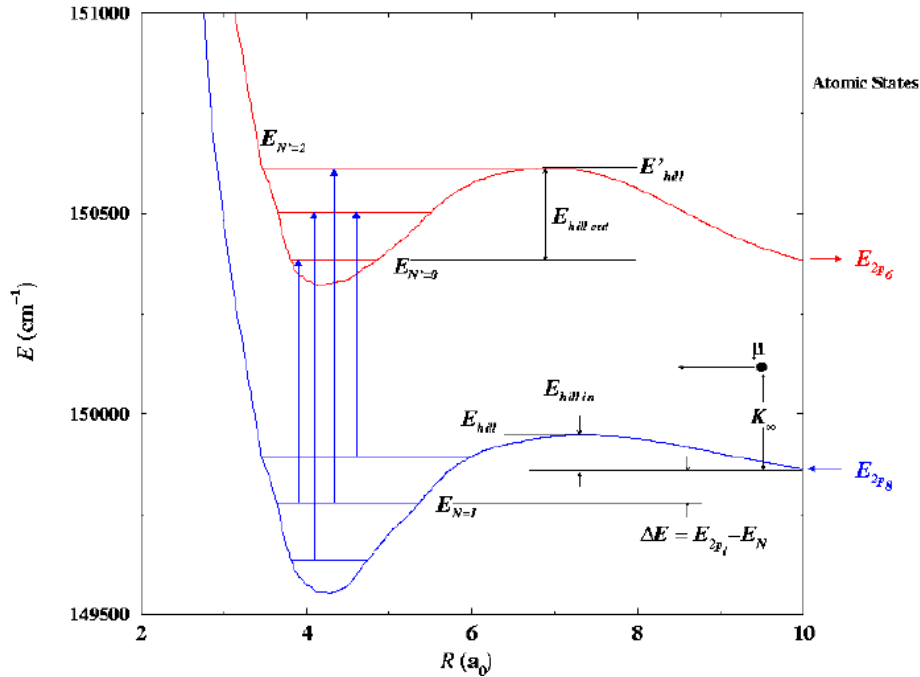
we also indicate the absolute uncertainty in the energy of a photon  $h\nu = |E_{N'} - E_N|$ , which is calculated as the sum of uncertainties  $\Delta_N$  (defined in equation (20)) in the energy of the vibrational-electronic states involved in a transition  $2p_i(J)\Omega^\pi N \rightarrow 2p_f(J')\Omega'^{\pi'} N'$ :

$$\Delta = \Delta_N + \Delta_{N'}. \quad (21)$$

Table 3 indicates that an infrared photon should be absorbed between  $(2p_i(J)\Omega^\pi N)$  states.

**Table 3:** The characteristics of transitions between vibrational-electronic states. The absolute uncertainty,  $\Delta$ , (from equation (21)) for the photon's energy  $h\nu$  and the relative uncertainty,  $\rho$ , in the energy of the photon are given.

Transition	$\Delta J$	$\Delta\Omega$	$N \rightarrow N'$	$h\nu$ ( $\text{cm}^{-1}$ )	$\lambda$ ( $10^{-6}$ m)	$\nu$ ( $10^{13}$ Hz)	$T$ ( $10^{-13}$ s)	$\rho$ (%)
$2p_8 \rightarrow 2p_6$	0	0	$0 \rightarrow 1$	$870 \pm 20$	$11.5 \pm 0.3$	$2.60 \pm 0.06$	$0.38 \pm 0.01$	2.3
			$1 \rightarrow 0$	$610 \pm 40$	$16 \pm 1$	$1.8 \pm 0.1$	$0.55 \pm 0.04$	6.6
			$1 \rightarrow 2$	$830 \pm 40$	$12.0 \pm 0.6$	$2.5 \pm 0.1$	$0.40 \pm 0.02$	4.8
			$2 \rightarrow 1$	$610 \pm 20$	$16.4 \pm 0.5$	$1.83 \pm 0.06$	$0.55 \pm 0.02$	3.3



**Figure 7:** Transitions between vibrational levels of the  $(2p_6(J=2)\Omega=2)$  (red line) and  $(2p_8(J=2)\Omega=2)$  (blue line) molecular states. The energies relevant for the discussions from sections 5 and 6 are indicated graphically.

Once a transition that satisfies the selection rules is identified, we must consider a “time of interaction”,  $\Delta t$ , spent by atoms in a molecular-vibrational region where the transition is allowed by the Franck-Condon principle. If  $\Delta R$  is the width of this region, and  $\nu$  is the speed of the reduced mass,  $\mu$ , with respect to CM (figure 2) then we have  $\Delta t = \Delta R/\nu$ . The speed,  $\nu$ , is related to the local kinetic energy,  $K$ , of the reduced mass when a transition occurs by the equation  $\nu = \sqrt{2K/\mu}$ , where

$$K = K_{\infty} + (E_{2p_i} - E_N). \quad (22)$$

In formula (22),  $K_{\infty}$  is the asymptotic kinetic energy, and  $E_{2p_i}$  is the atomic energy of the incoming collisional channel,  $2p_i$ . Finally, the time of interaction is

$$\Delta t = \Delta R \sqrt{\frac{\mu}{2(K_{\infty} + (E_{2p_i} - E_N))}}. \quad (23)$$

If we set  $K_{\infty} \approx 0$  in formula (23) then we find a maximum time of interaction,  $\Delta t_0$ . If  $K_{\infty} \approx 0$  and  $E_{2p_i} < E_N$  then the atoms cannot reach the vibrational region where the transition occurs, and  $\Delta t_0$  is undefined. If we set  $\Delta t = T$  (the period of a transition photon) in equation (23) and solve for  $K_{\infty}$  then the solution

$$E_{\text{limit}} = \frac{\mu(\Delta R)^2}{2T^2} + E_N - E_{2p_i} \quad (24)$$

represents the maximum asymptotic kinetic energy at which the transition occurs. An electronic-vibrational transition can occur if  $\Delta t > T$ . If we substitute both  $\Delta t$  (from equation (23)) and  $T$  (from equation (24)) in the inequality  $\Delta t < T$ , we get  $K_{\infty} > E_{\text{limit}}$ . In this case, the collision is too fast and the photon cannot be absorbed. If  $\Delta t_0 < T$  then the transition is too fast for any  $K_{\infty} > 0$ .

If there is a potential hill,  $E_{\text{hill in}}$ , in the incoming channel (see figure 7) then classically, the HeNe system may not have enough energy to get over this barrier and reach the molecular-vibrational region. In this case, according to the laws of classical physics the transition cannot take place. We say that a transition is classically “forbidden” for  $K_{\infty} < E_{\text{hill in}}$ . We can define a time  $\Delta t_{\text{hill in}}$  associated to this case which can be calculated when  $K_{\infty} = E_{\text{hill in}}$  in formula (23). If  $\Delta t_{\text{hill in}} < T$ , the transition is classically “forbidden”.

**Table 4:** Vibrational-electronic transitions between two molecular states ( $\Delta t_0 > T$ ). "Allowed" corresponds to  $\Delta t_{\text{hill in}} > T$  and "Forbidden" corresponds to  $\Delta t_{\text{hill in}} < T$ .

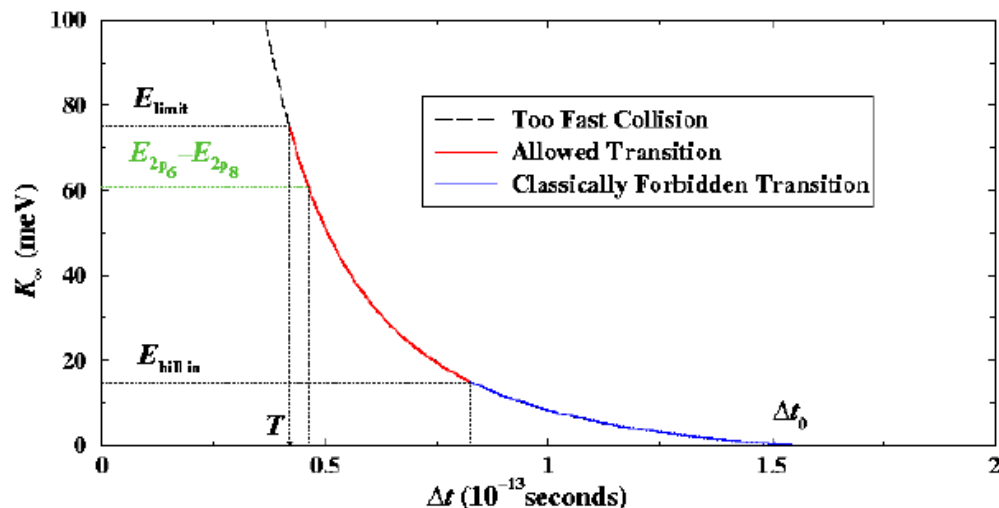
<i>Transition</i>	$\Delta J$	$\Delta \Omega$	$N \rightarrow N'$	$T$ ( $10^{-13}$ s)	$\Delta t_0$ ( $10^{-13}$ s)	$\Delta t_{\text{hill in}}$ ( $10^{-13}$ s)	<b>Status</b>
$2p_8 \rightarrow 2p_6$	0	0	0 $\rightarrow$ 1	0.3838	0.4207	0.3291	<i>Forbidden</i>
			1 $\rightarrow$ 0	0.5504	0.9385	0.5001	<i>Forbidden</i>
			1 $\rightarrow$ 2	0.4004	1.5522	0.8272	<i>Allowed</i>
			2 $\rightarrow$ 1	0.5468	undefined	1.0572	<i>Allowed</i>

Table 4 gives for the four vibrational transitions from table 3, the times discussed above. The transitions labeled "allowed" correspond to  $\Delta t_{\text{hill in}} > T$  (or  $E_{\text{limit}} > E_{\text{hill in}}$ ), and the transitions labeled "forbidden" correspond to  $\Delta t_{\text{hill in}} < T$  (or  $E_{\text{limit}} < E_{\text{hill in}}$ ). In the latter case, the transition can occur only *via* quantum tunneling in the incoming channel. With these results available, the experimentalists have the necessary information to identify a temporary HeNe molecule using an infrared laser spectroscopy technique.

### Experimental testing of the population of $\text{Ne}^*(2p_6)$ atoms

We propose a theoretical model able to predict the population of Neon atoms on the  $2p_6$  state after collision and stimulated absorption of an infrared photon from the  $2p_8$  state. Our model takes into consideration the quantum tunneling effect.

We take the test transition ( $2p_8(J=2)\Omega=2, N=2$ )  $\rightarrow$  ( $2p_6(J=2)\Omega=2, N=1$ ), because it has a potential hill in the incoming molecular channel (see figure 7). Figure 8 shows the relationship between  $K_\infty$  (given in units of meV, where  $1\text{meV} = 8.065\text{ cm}^{-1}$ , because they are used by experimentalists) and  $\Delta t$  from equation (23) for this transition.

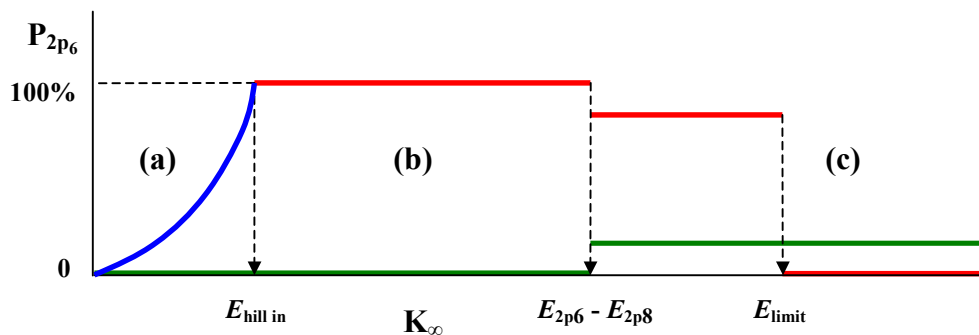


**Figure 8:** The relationship between the energy  $K_{\infty}$  and the time of interaction  $\Delta t$ .

The energy criterion discussed above leads to the following situations: (a) if  $K_{\infty} < 15\text{meV}$ , then the Frank-Condon region of the  $(2p_8(J=2)\Omega=2)$  channel can be accessed through quantum tunneling only. Consequently, the probability to excite  $\text{Ne}^*(2p_6)$  atoms is small as shown in figure 9(a), where we label by  $P_{2p_6}$  the population of  $\text{Ne}^*(2p_6)$  atoms relative to the initial population of the  $\text{Ne}^*(2p_8)$  atoms before collision. (b) If  $15\text{meV} < K_{\infty} < 75.1\text{meV}$ , then the transition is allowed and the entire population of  $\text{Ne}^*(2p_8)$  atoms is transferred on the  $2p_6$  state, as shown in figure 9(b). In this case the population of the  $\text{Ne}^*(2p_6)$  atoms is 100%. (c) If  $K_{\infty} > 75.1\text{meV}$ , then the collision is too fast and eventually no  $\text{Ne}^*(2p_6)$  atoms will form due to a vibrational-electronic transition as shown in figure 9(c). However, if a collision is more energetic than the energy difference between the (asymptotic) atomic levels (i.e.  $K_{\infty} > E_{2p_6} - E_{2p_8}$  of  $61\text{meV}$ ) it is possible to excite the  $\text{Ne}^*(2p_6)$  atoms at large internuclear distances ( $R > 12a_0$  in figure 4), *before* the molecular interaction between He and Ne atoms starts to play a role. The green line represents the population of  $\text{Ne}^*(2p_6)$  atoms due to a  $2p_8 \rightarrow 2p_6$  transition at large  $R$  and for large  $K_{\infty}$ .

The population of the  $\text{Ne}^*$  atoms after collision with He atoms and the absorption of an IR photon (figure 9) can be measured in an experiment of atomic spectroscopy of the emission lines. The  $\text{Ne}^*(2p_6)$  state discussed above is optically connected to the  $1s_2$  and  $1s_4$  states of the lower  $\text{Ne}^*(2p^53s)$  configuration. The intensity of the radiation emitted by spontaneous emission from the  $2p_6$  state is proportional with the population of the  $\text{Ne}^*(2p_6)$  atoms. Therefore, figure 9 implicitly shows the variation of the intensity we expect for a transition from the  $2p_6$  state toward a state of the  $\text{Ne}^*(2p^53s)$  configuration, which could be measured in a spectroscopic experiment.





**Figure 9:** Qualitative representation of the population of  $\text{Ne}^*(2p_6)$  atoms as a function of  $K_\infty$  for the transition  $(2p_8(J=2)\Omega=2, N=2) \rightarrow (2p_6(J=2)\Omega=2, N=1)$ .

## Conclusions

In this paper we develop a theoretical model able to predict states of vibration in a temporary molecule formed during a collision between two rare gases. To the best of our knowledge this is for the first time when modes of vibration are identified in a temporary molecule formed between He and Ne. Our model uses a parabolic approximation for a harmonic oscillatory motion in the first order and a Morse potential in the second order of calculations, which includes explicitly the effect of anharmonicity. In this study we choose the He-Ne system because of our success in explaining various atomic effects in He-Ne collisions [2-6] based on a reliable potential model [2]. This model can be applied to any similar collisions. We identified several vibrational–electronic transitions between molecular channels that can be investigated in spectroscopic measurements using the absorption of an infrared laser pulse. The laws of chemistry simply deny the formation of a molecule between two rare gas atoms. A successful experiment for the identification of vibrational states in a temporary HeNe molecule will revise this restrictive point of view. In addition, our model predicts the relative population of  $\text{Ne}^*$  atoms after collision, which is proportional with the intensity of the radiation released by atoms in spontaneous emissions. The intensity of an emission line is relatively easy to measure. We hope that our study will stimulate interest in the experimental identification of the HeNe molecule.

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