Vibrational spectra of N$_2$: An advanced undergraduate laboratory in atomic and molecular spectroscopy

S. B. Bayrama and M. V. Freamatb)

Physics Department, Miami University, Oxford, Ohio 45056

(Received 18 January 2012; accepted 12 May 2012)

We describe an advanced undergraduate experiment to demonstrate molecular spectroscopy by measuring the vibrational energy spacing of nitrogen molecules in the gas phase. We show how the use of a simple and readily available AC discharge tube and a handheld spectrometer allows students to observe and measure the radiative collisional phenomena in the gas, and to scrutinize the resulting emission spectrum for an instructive analysis of the quantized vibrational potential of neutral as well as ionized N$_2$. © 2012 American Association of Physics Teachers.

[http://dx.doi.org/10.1119/1.4722793]
freedom complicating even more the energy level diagram. However, these levels are much closer than the vibrational levels, such that they form only a band spectrum given the medium resolution of the experiment presented below.

B. Electric discharges in gases

To observe the vibrational levels, the nitrogen molecule must be first excited into metastable radiative states, such as via a transition from the molecular ground state $^1\Sigma_g$ into $^3\Pi_u$. There are several methods to achieve this. For instance, in our experiment, the students employ the transfer of energy from a metastable state of argon atoms to the ground state of $N_2$ in a discharge tube. We realized that the experimental setup and control can be made particularly simple if one uses a commercially available AC capillary discharge tube instead of the more complex DC discharge tube formerly serving the same goal in our spectroscopy course. Moreover, although the DC discharge may result in cleaner spectra, the spectra collected from the AC discharge tube exhibit one additional line involving a $N_2^+$ ion vibrational state. This extra feature adds to the richness of the physics behind the data and promotes discussions and active learning about the influence on vibrational states due to a change in the number of electrons rather than electron occupancy alone.

Electric discharge tubes use high voltages applied between two electrodes placed in a low pressure gaseous environment determining a collisional electric breakdown of some of the atoms and molecules of the gas into a plasma of electron-ion pairs, and excited species that decay by emission of light forming a glow discharge. As long as the potential difference is maintained, the plasma is self-sustaining, because the accelerated free electrons are involved in new impact excitations and ionizations, while the ions are accelerated and bombard the cathode releasing new electrons. Because the concentration of electrons in the cathode region is much higher due to this continuous electron multiplication, most of the electron impact excitations take place in a negative glow occurring in the vicinity of the cathode. The negative glow is characterized by a brighter light, the color of which depends on the nature of the discharge gas. As the electrons travel through the negative glow away from the cathode, their energy drains until it gets too low for impact excitations yielding a gradually dimmer light intensity in the middle of the tube. Consequently, the most active discharge region to be probed spectroscopically for populated metastable excited states is in the proximity of the cathode where electron-impact excitations are upheld.

In a DC discharge, the negative glow is localized close to the electrode serving as a cathode. In an AC discharge, the negative glow develops next to both electrodes, as they take turns at playing the roles of cathode and anode. In this case, the oscillating electric field provides an extra source of ionization power for the slower electrons in the plasma, enhancing the efficiency of the discharge. This may explain the more probable occurrence of $N_2^+$ ionizations leading to the extra peak in the spectrum obtained when the students probe the AC tubes, compared to the DC-tube spectra.

C. Experiment

Most commercial discharge tubes have some minute contamination with other gases. In our experiment, the presence of a small amount of argon in the commercial nitrogen AC discharge tubes is instrumental. The electron impact with argon atoms in the ground state populates the two metastable levels of configuration $3p^44s$ at 11.55 eV and 11.72 eV. When the argon excited into these metastable states ($Ar^+(M)$) is mixed with the neutral molecular nitrogen $N_2$ in its vibrational ground state $^1\Sigma_g$, the nitrogen gets excited into one of the levels $v'$ of the $C^3\Pi_u$ state because the energy
of the argon metastable states matches the necessary excitation energy of 11.1 eV

\[ \text{Ar}^*(M) + \text{N}_2(X,v = 0) \rightarrow \text{N}_2(C,v') + \text{Ar}. \]  

(1)

The discharge region may also contain other species of molecular nitrogen, such as positive ions (N2+) produced by direct electron impact ionization of the neutral molecules from ground state \( \bar{X}^1\Sigma_g^+ \) (predominant in the gas). Depending on the energy of the impact electron, the ions may be knocked either into their vibrational ground state \( \bar{X}^1\Sigma_g^+ \) (which could be subsequently excited) or directly into an excited \( \bar{B}^2\Sigma_u^+ \) state13

\[ \text{N}_2(X,v = 0) + e \rightarrow \text{N}_2^+(X,v') + 2e \]  

(electron energy > 15.6 eV),

(2)

\[ \text{N}_2(X,v = 0) + e \rightarrow \text{N}_2^+(B,v') + 2e \]  

(electron energy > 18.5 eV).

(3)

Subsequently, the excited states decay spontaneously, spawning an emission spectrum with the line intensities proportional to the population of the upper bands \( \text{N}_2(C,v') \) or \( \text{N}_2^+(B,v) \)

\[ \text{N}_2(C,v') \rightarrow \text{N}_2(B,v'') + h\nu, \]  

(4)

\[ \text{N}_2^+(B,v') \rightarrow \text{N}_2^+(X,v'') + h\nu. \]  

(5)

In our experimental arrangement, the students are required to probe the negative glow of the AC capillary tube using a tube \( \rightarrow \) fibre \( \rightarrow \) Ocean Optics-UV-VIS spectrometer system with a resolution of 0.5 nm [Fig. 1(a)]. The vibronic radiative transitions occurring between various vibrational states of \( \text{N}_2 \) and \( \text{N}_2^+ \) are recorded into a spectrum representing the emission bands in the 300–480 nm range, as exemplified in Fig. 2(a). The students are thereafter expected to analyze the data thoroughly within the conceptual framework introduced in the lecture part of the course, furnished with hand-outs of \( \text{N}_2 \) and \( \text{N}_2^+ \) potential energy curves, argon Grotrian diagram, Franck-Condon factors, and transition intensity ratios.10,14,15

### III. GUIDE TO THE ANALYSIS OF SPECTRA

#### A. Tallying up the data

The emission spectrum of \( \text{N}_2 \) is a seedbed of information about the potentials associated with the vibrational states of the diatomic molecules. Hence, the students are first required to extract and organize the transition characteristics from the spectrum.

To correctly read it, and thereupon lay out and interpret the data, the students must be familiarized with the selection rules governing the transitions leading to the pattern of intensity peaks within each emission band progression. Thus, besides evident contributions, such as the electron occupancy of level \( v' \) and the electronic transition probability (constant for transitions within the same system, like the second positive system

![Fig. 2. (Color online) (a) A typical emission spectrum from the discharge tube, exhibiting both \( \text{N}_2(C^1\Pi \rightarrow B^3\Pi) \) and \( \text{N}_2^+(B^2\Sigma \rightarrow X^2\Sigma) \) radiative decays, with assigned vibrational quantum numbers \( v' - v'' \). (b) Vibrational energy level diagram for the \( \text{N}_2 \) transitions represented by the shown spectrum. The transition arrows are arranged in sequences of constant \( \Delta v \), vertically aligned with the respective spectral bands.](image)
Table I. Franck-Condon factors ($\times 10^5$) for the observed $N_2$ vibrational transitions of the second positive system.

<table>
<thead>
<tr>
<th>$v'$</th>
<th>$v''$</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td></td>
<td>4527</td>
<td>3291</td>
<td>1462</td>
<td>517.2</td>
<td>158.8</td>
<td>45.4</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td>3949</td>
<td>2157</td>
<td>2033</td>
<td>1989</td>
<td>1097</td>
<td>466.3</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>1330</td>
<td>3413</td>
<td>238.4</td>
<td>634.4</td>
<td>1605</td>
<td>1393</td>
</tr>
</tbody>
</table>

C$^3\Pi_u \rightarrow B^3\Pi_g$), the transition probability between vibrational levels depends on the degree of overlap of the wave functions of the two states. The overlap is quantified by Franck-Condon factors weighting the vibronic transition probability.

As shown in Table I for the second positive system, these factors take dissimilar values for distinct pairs of vibrational states $v' \rightarrow v''$, causing trends in the spectral intensities easily identifiable on the actual spectrum. For instance, whereas the $(v' = 0) \rightarrow (v'' = 0, 1, 2, \ldots)$ transitions have decreasing intensities, the $v' > 0$ progressions have two local intensity maxima (corresponding to decays from the two vibrational turning points of the respective $v'$ level). Once the transitions are recognized and assigned, in order to provide and verify the ingredients for further analysis, the students are required to build vibrational energy level diagrams and Deslandres tables of wave numbers $\nu$ for the two radiative systems, $N_2$ and $N_2^+$, as exemplified in Fig. 2(b) and Table II.

B. Harmonic vs anharmonic vibrations

It is enticing to think about the $N_2$ diatomic molecule as two particles connected by a spring performing simple harmonic oscillations (as represented in Fig. 1) described by a quadratic potential. In reality, the molecular potential is not harmonic, and the total potential of a stationary bonding configuration—including the energy of the electrons and the repulsive Coulomb interaction between the nuclei—depends on the internuclear distance asymmetrically, as depicted in Fig. 3: the steeper curve at smaller separations indicates that the nuclei spend less time there, that is, the probability to find the molecule compressed is somewhat less than stretched. It’s thence noteworthy that the parabolic harmonic potential is still a good model for the lowest vibrational states where the curve becomes symmetric, especially for nitrogen due to its deep potential well.

Concretely, ignoring the densely packed energy levels introduced by the rotational levels, the wavefunction $\psi(r)$ for both nuclei expressed in the center of mass frame results solely in terms of the displacement with respect to equilibrium bond separation $r - r_0$ from

$$
\left[ -\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + V(r) \right] \psi(r) = E \psi(r),
$$

with $\mu = m_N/2 = 1.16 \times 10^{-26}$ kg being the reduced mass of the $N_2$ molecule. The asymmetrical $V(r)$ can be emulated by a Morse potential:

$$
V(r) = D_e \left( 1 - e^{-\beta(r-r_0)} \right)^2,
$$

where $D_e$ is the dissociation energy given by the depth of the potential well, and $\beta$ relates to the force constant $k_0$ of the bond at equilibrium via $k_0 = 2D_e \beta^2$. Solving Eq. (6) with this potential, one can find the energy $E_v$ of each vibrational level $v$

$$
E_v/\hbar c = \omega_0 \left( v + \frac{1}{2} \right) - \omega_0 \omega_0 \left( v + \frac{1}{2} \right)^2,
$$

where $\omega_0$ (calculated in cm$^{-1}$) is the fundamental frequency of the vibration, naturally related with the other parameters of the oscillator

$$
\omega_0 = \frac{1}{2\pi c} \sqrt{\frac{k_0}{\mu}}\frac{\beta}{c} \sqrt{\frac{D_e}{2\pi^2 \mu}}.
$$

Because the product $\omega_0 \omega_0 \omega_0$ quantifies the first order energy deviation from that of a harmonic oscillator, it is termed anharmonicity. Based on Eq. (8), the students can conveniently express the photon wave numbers $\nu_{v'v''}$ (tabulated in the Deslandres table) in terms of $\omega_0$ and $\omega_0 \omega_0 \omega_0$ for various transitions, conducive to evaluating the harmonic and anharmonic characteristics of the two states implicated, and thereof the merits of the harmonic approximation for the molecular oscillator. Thus, one has to notice first that the vibrational levels are superimposed over the respective electronic level $E_v$, such that the net energy is given by $E = E_v + E_x$, where the energy of the electronic level can be also rescaled to cm$^{-1}$ via $E_v/\hbar c$. Therefore, the energy difference between
the various pairs of vibrational levels \( v' \rightarrow v'' \) implicated in the transitions recorded by the spectrum is

\[
\tilde{v}_{v'v''} = \frac{\Delta E}{\hbar c} = \frac{\Delta E_{el}}{\hbar c} + \left( \frac{E_e - E_{el}}{\hbar c} \right) \\
= \omega_{el} + \omega_0' \left[ \left( v' + \frac{1}{2} \right) - x_0' \left( v' + \frac{1}{2} \right)^2 \right] \\
- \omega_0'' \left[ \left( v'' + \frac{1}{2} \right) - x_0'' \left( v'' + \frac{1}{2} \right)^2 \right]. \quad (10)
\]

For instance, because the most intense spectral line on the exemplified spectrum occurs due to transitions between the vibrational zero-point levels \((v', v'') = (0, 0)\) of the two electronic states \(C^1\Pi_g \rightarrow B^3\Pi_u\), Eq. (10) adapted explicitly to this line takes the form

\[
\tilde{v}_{00} = \omega_{el} + \frac{1}{2} (\omega_C - \omega_B) - \frac{1}{4} (\omega_C x_C - \omega_B x_B). \quad (11)
\]

Therefore, combining and rearranging Eqs. (10) and (11), one finds for arbitrary transitions that

\[
\tilde{v}_{v'v''} = \tilde{v}_{00} + \omega_C v' - \omega_C x_C(v' + 1) v' \\
- [\omega_B v'' - \omega_B x_B(v'' + 1) v'']. \quad (12)
\]

Henceforth, with five terms from the Deslandres tables (that is, five assigned spectral lines), the students can calculate algebraically the fundamental frequencies \(\omega_C, \omega_B\) of the two electronic states, and the respective anharmonicities, \(\omega_C x_C\) and \(\omega_B x_B\). Moreover, the frequencies will further give the force constants in the two states, \(k_0 = 4\pi^2 \omega_0^2 C^2\mu\). For instance, based on the wave numbers for the most intense progression \((v' = 0) \rightarrow (v'' = 0, 1, 2)\) stored in the Deslandres table, the students can estimate the parameters of the \(B^3\Pi_u\) potential from the linear system

\[
\begin{cases}
\omega_B - 2\omega_B x_B = \tilde{v}_{00} - \tilde{v}_{01}; \\
2\omega_B - 6\omega_B x_B = \tilde{v}_{00} - \tilde{v}_{02}.
\end{cases} \quad (13)
\]

The results are subsequently compared to the values published in the literature, as exemplified in Table III where the molecular parameters of state \(B^3\Pi_u\) calculated using the wave numbers in Table II show good agreement with published data.\(^{10,14}\)

Moreover, this analysis provides a framework for the students to confirm the validity of the harmonic model for the vibrations of \(N_2\): not only that the anharmonic term can be safely neglected for small \(v\) but also Eq. (10) offers a quantitative confirmation. Thus, by subtracting the energies of successive levels \(v\) within a state characterized by \((\omega_0, \omega_0 x_0)\), one obtains the vibrational energy spacing,

\[
\Delta E_v/\hbar c = \Delta \tilde{v} = \omega_0 - 2\omega_0 x_0 (v + 1), \quad (14)
\]

which suggests that the energy steps are fairly constant at low \(v\), as confirmed experimentally by the regularity of the spectrum peaks within each progression and the inter-level energies listed in Fig. 2(b), but reduce gradually at high \(v\), up to a maximum level \(v_{\text{max}} = 1/2x - 1\) corresponding to the dissociation energy \(D_e\). This argument stays behind the so-called Birge-Sponer treatment\(^{17-19}\) that uses the linear plot of \(\Delta E_v\) against \((v + 1)\) to find the dissociation energy \(D_0\) with respect to the zero-point level, simply given by the area under the linear plot in the interval \((0, v_{\text{max}})\). Because \(\Delta E_0/\hbar c \approx \omega_0\), whereas \(\Delta E_{v_{\text{max}}} \rightarrow 0\), the zero-point dissociation energy is \(D_0/\hbar c = \omega_0^2/4\omega_0 x_0\). Combining with Eq. (8), the students can furthermore calculate the dissociation energy \(D_e\) relative to the equilibrium point (that is, the bottom of the potential well, as shown in Fig. 3)

\[
D_e/\hbar c = \frac{E_0}{\hbar c} + \frac{D_0}{\hbar c} = \frac{1}{2} \omega_0 - \frac{1}{4} \omega_0 x_0 + \omega_0^2/4\omega_0 x_0. \quad (15)
\]

Insofar as \(D_e\) and \(\omega_0\) can be substituted in Eq. (9) to find \(\beta\), this concludes the characterization of the \(B^3\Pi_u\) state, and the students can substitute the values and plot the Morse potential to visualize the asymmetric potential.

To characterize the excited \(C^1\Pi_u\) state in the same fashion, Table II has to be completed with the wave numbers for \(v' > 0\), providing the extra terms in Eq. (12) necessary to find first \(\omega_C, \omega_B x_C\), and then the respective force constant and dissociation energy of the excited state, as well as the energy difference \(\Delta E_{el} = \hbar c k_0\) between the \(C^1\Pi_u\) electronic states, via Eq. (11). Additionally, because the spectrum also exhibits three transition lines of the ionized molecule \(N_2^+\), between the zero point of \(B^3\Sigma_u^+\) to the ground state \(\Sigma^2\Sigma_g^+\), the strategy delineated above can be applied once again to characterize the \(X^2\Sigma_g^+\) ionic ground state potential, and then estimate the ionization energies of \(N_2\) from various vibrational levels within the second positive system.

C. Adapting to a broader audience

While the analysis sketched above is suited to our advanced spectroscopy course, the experiment can be streamlined into a qualitative demonstration of quantum mechanical phenomenology for an inexpert audience. The setup is simple and portable, and an adequate, albeit coarse, spectrum can be readily visualized on a computer screen to illustrate both the electron impact excitations and the vibrational decays in gases—subjects relevant in introductory courses in general physics, modern physics, meteorology, and astronomy. For instance, the calculus-based introductory physics course offered by our department dedicates three weeks to quantum mechanics with brief topical excursions into molecular vibrations, excited atomic and molecular states, and emission spectra.\(^{20}\)

IV. CONCLUSIONS

We have described a relatively simple and affordable advanced laboratory experiment to demonstrate vibrational emission spectra stimulated by an electron-impact technique. The experiment—greatly mobile and adaptable for pedagogical applications involving students with a variety of backgrounds—employs a molecular nitrogen AC-discharge capillary tube and a handheld Ocean Optics spectrometer. The students use the optical fibre of the spectrometer to probe the negative glow of the tube where \(N_2\) gets most abundantly excited by
impact excitations. Although it is too rough to discern the fine structure of rotational levels, the 0.5 nm resolution is sufficient to observe and record the $C^3\Pi_u \rightarrow B^3\Pi_g$ vibrational emission bands in the spectral range between 300 and 480 nm, as well as the spectral signature of some low level $\text{N}_2^+$ radiative decays. The spectrum is subsequently used in conjunction with guiding materials to systematically extract, format, and analyze information regarding the vibration of $\text{N}_2$, representative for homonuclear diatomic molecules. Thus, the students scrutinize the spectrum and assign spectral lines based on transition probabilities, measure vibrational energy spacings and draw transition diagrams, construct and verify tables of transition energies and wave numbers, adapt the quantum mechanical equations of the molecular vibrator to the concrete data, calculate the constants characterizing the implicated vibrational potentials, and evaluate the merits and limits of the simple harmonic oscillator model in describing the behaviour of the quantum oscillator in the observed modes. In the context of the advanced spectroscopy course in our department, this experiment succeeds a Raman scattering measurement of liquid-phase nitrogen vibrations and precedes a complementary measurement of the rotational structure of $\text{N}_2^+$, parts of an ensemble of laboratory exercises in atomic and molecular physics designed to offer our students a strong background in a chapter of concepts and techniques indispensable for any physics graduate.

ACKNOWLEDGMENTS

Financial support from the Research Corporation and the Dean of the College of Arts and Science at Miami University are gratefully acknowledged for seed funding the spectroscopy lab. The authors also wish to thank David Fisher for his valuable suggestions.

\begin{itemize}
\item[a)] Electronic mail: bayransb@muohio.edu
\item[b)] Electronic mail: freamams@muohio.edu
\end{itemize}