Vibrational spectra of N_2: An advanced undergraduate laboratory in atomic and molecular spectroscopy

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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.*
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I. INTRODUCTION

Experimental explorations in instructional laboratories of molecular spectroscopy are instrumental not only in educating students about the quantum mechanical phenomenology ingrained into the microscopic structure of matter but also in familiarizing them with the germinal scientific puzzles and revolutionary answers that historically led to the discovery of quantum mechanics. Furthermore, the substances under spectroscopic scrutiny are often of particular interest in wider contexts. For instance, the experiment described here uses molecular nitrogen, a predominant constituent of Earth's atmosphere, which plays a central role in auroras and airglows,[1] as well as in physical phenomena of environmental concern,[2] such as the photochemical formation of nitrogen oxides which catalyse the destruction of stratospheric ozone.[3] Also, the fact that the collisional properties of nitrogen are employed in glow discharge plasma nitriding—a technique used to improve the mechanical properties of materials, especially iron-based alloys[4]—is likely to raise the attention of students planning for careers in applied science and engineering. Hence, the importance of atomic, molecular, and optical physics in science education cannot be overemphasized.[5] Consequently, a great deal of effort was directed in our department toward maintaining an advanced laboratory course focused on spectroscopy of atoms and molecules, for a diverse and solid education of our upper-level physics majors.[6,7] We hope that the broad training and practical skills that our students receive from the experiments performed in the sound pedagogical settings of this course will contribute to their strong background as they pursue industrial and governmental careers, or carry on in academic graduate programs.

The backbone of the course is a series of atomic and molecular spectroscopy experiments designed to reinforce the topical material and familiarize the students with some specific research techniques. The lab reports are used as formative assessment tools to develop the students' scientific writing skills. In this article, we introduce one of these experiments: an investigation of the electron-impact vibrational excitations in the diatomic nitrogen molecule, N_2. The experiment was recently redesigned in order to focus the students' attention onto the physics behind the phenomenon rather than irrelevant experimental minutia, as well as to make it tractable enough to be used as a readily available demonstration even in introductory courses. Notwithstanding its relatively simple setup, this experiment offers significant insight into a range of spectroscopic and quantum mechanical concepts and applications such as: the concrete measurement of gaseous emission spectra; the diatomic molecular orbitals and the respective superimposed structure of electronic and vibrational energy levels with standard spectroscopic notations; the electron occupancy, excitations and transitions between radiative vibronic states; the deviation of the data from the models used to emulate the bonding potential in the molecule; and so on.

II. TOPICAL BACKGROUND AND EXPERIMENT

Historically, the vibrational and rotational spectra of diatomic molecules have played a central role in testing the consistency of quantum mechanics. True to this legacy, we report a relatively straightforward and affordable experiment to study a vibrational molecular structure from spectra collected from diatomic nitrogen sustaining electron-impact excitation in a commercial AC nitrogen discharge tube.

A. Electronic and vibrational structure of N_2

Homonuclear diatomic molecules provide an excellent basis for understanding the makeup of molecular orbitals by combinations of atomic orbitals: wave functions superposed linearly either constructively (bonding orbitals) or destructively (antibonding orbital), as governed by the symmetry of the molecule and the degree of atomic overlap.[8,9] Atomic orbitals may mix into molecular orbitals symmetric (σ) or asymmetric (π) under *rotations* about the internuclear axis. Also, molecular orbitals may be symmetric (g) or asymmetric (u) under *inversions* about the center of mass of the molecule. For instance, in the case of nitrogen, the $1s$ electrons are screened and localized, so their orbitals do not overlap effectively. In turn, the remaining 10 valence electrons occupy molecular orbitals resulting from mixing the atomic orbitals $2s$ and $2p$, including s–p interactions due to their proximity, as shown in Fig. 1(b). The discrete electron energy structure of the molecule is furthermore split into the superimposed fine spectrum of *vibrational* states. Because each electronic state is characterized by a different bond length and strength due to the various electron distributions, the molecular oscillator will have a variety of potential energy curves associated with distinctive vibrational states, each with a range of differently spaced vibrational levels, indexed by sets of quantum numbers $v = 0, 1, 2, \ldots$. Figure 3 illustrates two such potential curves[10] for the so-called second positive system of vibrational states: $C^3\Pi_u$ and $B^3\Pi_g$. The molecule also has quantized *rotational* degrees of

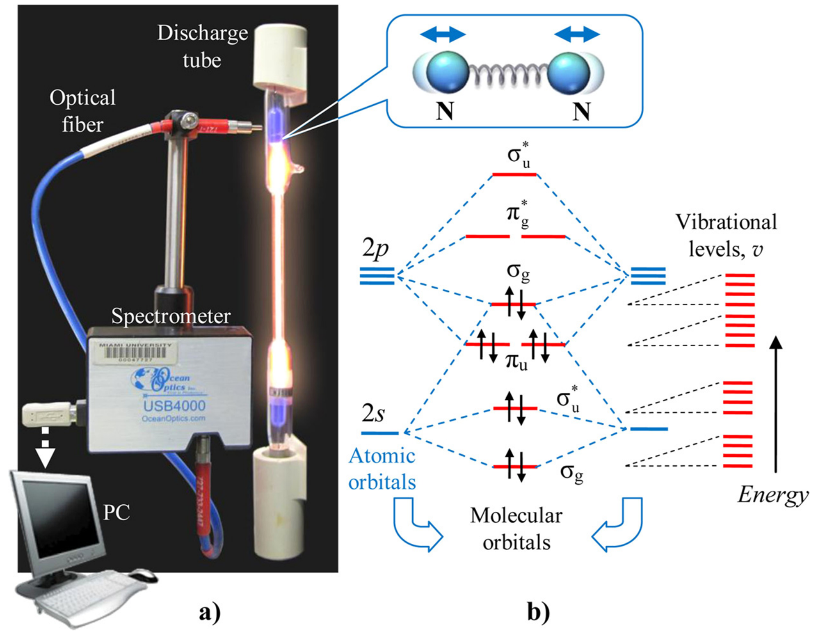

Fig. 1. (Color online) (a) In a simple experimental arrangement, the discharge capillary tube containing diatomic nitrogen gas is probed using the Ocean Optics-UV-VIS miniature spectrometer system. (b) The molecules of nitrogen perform vibrations as fashioned by the particular electron occupancy of bonding versus anti-bonding (*) molecular orbitals determining the length and strength of the bond. The energy levels of the corresponding quantized vibration of the molecule, described by the vibrational quantum number v, are superimposed over the electronic energy levels.

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 $X^1\Sigma_g$ into $C^3\Pi_u$. There are several methods to achieve this.[11] 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.[6] 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,[12] 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 $3p^54s$ at 11.55 eV and 11.72 eV. When the argon excited into these metastable states $(\mathrm{Ar}^*(M))$ is mixed with the neutral molecular nitrogen N_2 in its vibrational ground state $X^1\Sigma_g$, 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

$$\mathrm{Ar}^*(M) + \mathrm{N}_2(X, v = 0) \rightarrow \mathrm{N}_2(C, v') + \mathrm{Ar}. \tag{1}$$

The discharge region may also contain other species of molecular nitrogen, such as positive ions (N_2^+) produced by direct electron impact ionization of the neutral molecules from ground state $X^1\Sigma_g$ (predominant in the gas). Depending on the energy of the impact electron, the ions may be knocked either into their vibrational ground state $X^2\Sigma_g$ (which could be subsequently excited) or directly into an excited $B^2\Sigma_u$ state[13]

$$\mathrm{N}_2(X, v = 0) + e \rightarrow \mathrm{N}_2^+(X, v') + 2e \tag{2}$$

$$(\text{electron energy} > 15.6\,\mathrm{eV}),$$

$$\mathrm{N}_2(X, v = 0) + e \rightarrow \mathrm{N}_2^+(B, v') + 2e \tag{3}$$

$$(\text{electron energy} > 18.5\,\mathrm{eV}).$$

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

$$\mathrm{N}_2(C, v') \rightarrow \mathrm{N}_2(B, v'') + h\nu, \tag{4}$$

$$\mathrm{N}_2^+(B, v') \rightarrow \mathrm{N}_2^+(X, v'') + h\nu. \tag{5}$$

In our experimental arrangement, the students are required to probe the negative glow of the AC capillary tube using a tube → fibre → 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 N_2 and 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 N_2 and 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 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

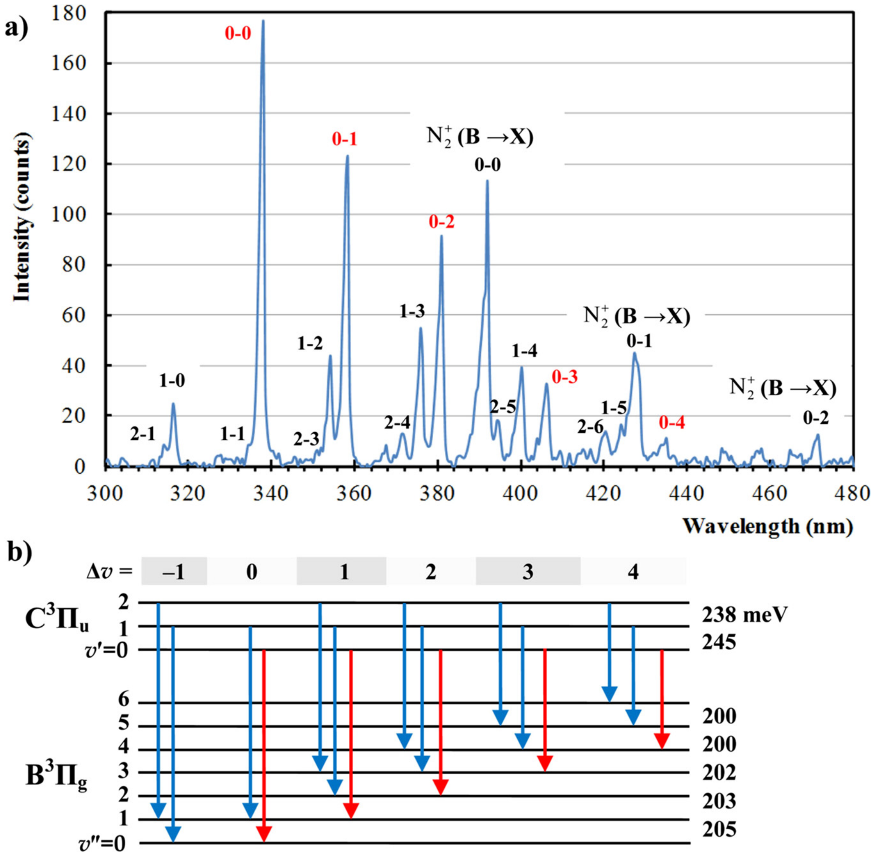

Fig. 2. (Color online) (a) A typical emission spectrum from the discharge tube, exhibiting both $\mathrm{N}_2(C^3\Pi \rightarrow B^3\Pi)$ and $\mathrm{N}_2^+(B^2\Sigma \rightarrow X^2\Sigma)$ radiative decays, with assigned vibrational quantum numbers $v' - v''$. (b) Vibrational energy level diagram for the N_2 transitions represented by the shown spectrum. The transition arrows are arranged in sequences of constant Δv, vertically aligned with the respective spectral bands.

Table I. Franck-Condon factors ($\times 10^4$) for the observed N_2 vibrational transitions of the second positive system.

v' \ v''	0	1	2	3	4	5
0	4527	3291	1462	517.2	158.8	45.4
1	3949	215.7	2033	1989	1097	466.3
2	1330	3413	238.4	634.4	1605	1393

$C^3\Pi_u \rightarrow B^3\Pi_g$), 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 $(v' = 0) \rightarrow (v'' = 0, 1, 2...)$ 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 $\tilde{\nu}$ 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.

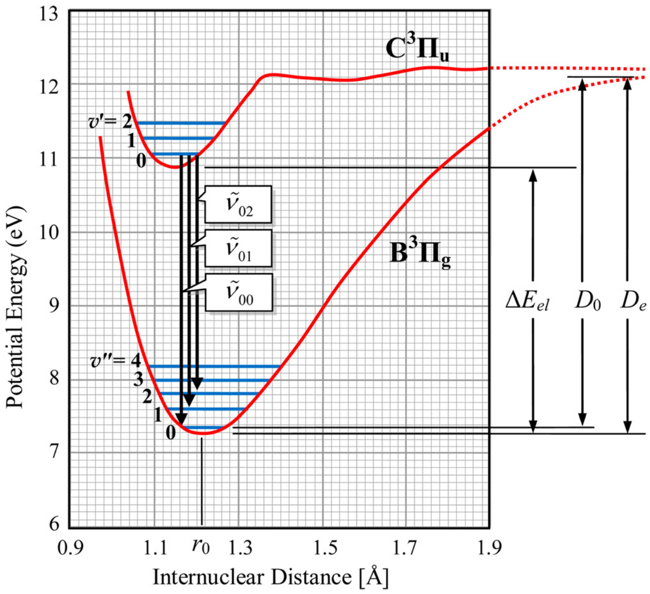

Fig. 3. (Color online) The potential energy curves (Ref. 10) for the nitrogen vibrational states $C^3\Pi$ and $B^3\Pi$ exemplified in this paper. The transitions responsible for the most intense peaks observed in the spectrum are also shown, indicated by the respective wave numbers $\tilde{\nu}_{0v''}$. The spectral analysis provides estimates for the energy difference ΔE_{el} between electronic states, and the dissociation energies $D_{0,e}$ for each electronic state.

Table II. Sample Deslandres table for the $(v' = 0) \rightarrow (v'' = 0..3)$ transitions of N_2. The table is filled with photon wave numbers $\tilde{\nu}_{v'v''} = \lambda^{-1}_{v'v''}$ (in cm^{-1}) extracted from the spectrum, and provides a verification tool, because the differences between successive columns and rows are to be constant for a correct assignment of band progressions.

v' \ v''	0	0–1	1	1–2	2	2–3	3
0	29598 $\tilde{\nu}_{00}$	1679	27919 $\tilde{\nu}_{01}$	1655	26264 $\tilde{\nu}_{02}$	1640	24629 $\tilde{\nu}_{03}$

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

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + V(r)\right]\psi(r) = E\psi(r), \tag{6}$$

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:[16–18]

$$V(r) = D_e(1 - e^{-\beta(r-r_0)})^2, \tag{7}$$

where D_e is the dissociation energy given by the depth of the potential well, and β 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

$$E_v/hc = \omega_0\left(v + \frac{1}{2}\right) - \omega_0 x_0\left(v + \frac{1}{2}\right)^2, \tag{8}$$

where ω_0 (calculated in cm^{-1}) is the fundamental frequency of the vibration, naturally related with the other parameters of the oscillator

$$\omega_0 = \frac{1}{2\pi c}\sqrt{\frac{k_0}{\mu}} = \frac{\beta}{c}\sqrt{\frac{D_e}{2\pi^2\mu}}. \tag{9}$$

Because the product $\omega_0 x_0$ 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 $\tilde{\nu}_{v'v''}$ (tabulated in the Deslandres table) in terms of ω_0 and $\omega_0 x_0$ 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_{el}, such that the net energy is given by $E = E_{el} + E_v$, where the energy of the electronic level can be also rescaled to cm^{-1} via E_{el}/hc. Therefore, the energy difference between the various pairs of vibrational levels $v' \rightarrow v''$ implicated in the transitions recorded by the spectrum is

$$\begin{aligned}\tilde{\nu}_{v'v''} &= \frac{\Delta E}{hc} = \frac{\Delta E_{el}}{hc} + \left(\frac{E_{v'}}{hc} - \frac{E_{v''}}{hc}\right)\\ &= \omega_{el} + \omega_0'\left[\left(v' + \frac{1}{2}\right) - x_0'\left(v' + \frac{1}{2}\right)^2\right]\\ &\quad - \omega''_0\left[\left(v'' + \frac{1}{2}\right) - x_0''\left(v'' + \frac{1}{2}\right)^2\right].\end{aligned} \tag{10}$$

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 $C^3\Pi_u \rightarrow B^3\Pi_g$, Eq. (10) adapted explicitly to this line takes the form

$$\tilde{\nu}_{00} = \omega_{el} + \frac{1}{2}(\omega_C - \omega_B) - \frac{1}{4}(\omega_C x_C - \omega_B x_B). \tag{11}$$

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

$$\begin{aligned}\tilde{\nu}_{v'v''} &= \tilde{\nu}_{00} + \omega_C v' - \omega_C x_C (v'+1)v'\\ &\quad - [\omega_B v'' - \omega_B x_B (v''+1)v''].\end{aligned} \tag{12}$$

Henceforth, with five terms from the Deslandres tables (that is, five assigned spectral lines), the students can calculate algebraically the fundamental frequencies $\omega_{C,B}$ 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 $B^3\Pi_g$ potential from the linear system

$$\begin{cases}\omega_B - 2\omega_B x_B = \tilde{\nu}_{00} - \tilde{\nu}_{01};\\ 2\omega_B - 6\omega_B x_B = \tilde{\nu}_{00} - \tilde{\nu}_{02}.\end{cases} \tag{13}$$

The results are subsequently compared to the values published in the literature, as exemplified in Table III where the molecular parameters of state $B^3\Pi_g$ 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 anharmonicity 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,

$$\Delta E_v/hc = \Delta\tilde{\nu} = \omega_0 - 2\omega_0 x_0(v+1), \tag{14}$$

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 $v_{max} = 1/2x - 1$ 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 ΔE_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 $(0, v_{max})$. Because $\Delta E_0/hc \approx \omega_0$, whereas $\Delta E_{v_{max}} \rightarrow 0$, the zero-point dissociation energy is $D_0/hc = \omega_0^2/4\omega_0 x_0$. 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)

$$\frac{D_e}{hc} = \frac{E_0}{hc} + \frac{D_0}{hc} = \frac{1}{2}\omega_0 - \frac{1}{4}\omega_0 x_0 + \frac{\omega_0^2}{4\omega_0 x_0}. \tag{15}$$

Insofar as D_e and ω_0 can be substituted in Eq. (9) to find β, this concludes the characterization of the $B^3\Pi_g$ state, and the students can substitute the values and plot the Morse potential to visualize the asymmetric potential.

To characterize the excited $C^3\Pi_u$ 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 $\Delta E_{el} = hc\omega_{el}$ between the C– B 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 $B^2\Sigma_u$ to the ground state $X^2\Sigma_g$, 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.

Table III. The analyzing of the sample emission spectrum in Fig. 2(a) yields molecular constants for the $B^3\Pi_g$ close to the values published in the literature (Refs. 10 and 14, and 15).

Constants	ω_0 (cm^{-1})	$\omega_0 x_0$ (cm^{-1})	k_0 (N/m)	D_e (eV)
Students	1703	12.1	1193	7.45
Literature	1730	14.1	1235	7.37

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 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 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 N_2^+, parts of an ensemble of laboratory exercises in atomic and molecular physics[6] designed to offer our students a strong background in a chapter of concepts and techniques indispensable for any physics graduate.

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[1] J. W. Chamberlain, *Physics of the Aurora and Airglow* (American Geophysical Union, Washington, DC, 1961).

[2] J. L. Hatfield and R. F. Follet, *Nitrogen in the Environment: Sources, Problems, and Management*, 2nd. ed. (Elsevier, Inc., Oxford, UK, 2008).

[3] S. S. Prasad and E. C. Zipf, "Photochemical production of odd nitrogen directly from O_2, N_2 principals: Atmospheric implications and related open issues," J. Geophys. Res. **109**, D08310, doi:10.1029/2003JD004061 (2004).

[4] A. Alsaran and A. Çelik, "Structural characterization of ion-nitrided AISI 5140 low-alloy steel," Mater. Charact. **47**, 207–213 (2001).

[5] National Research Council, *Atomic, Molecular, and Optical Science: An Investment in the Future* (National Academy Press, Washington, DC, 1994).

[6] J. Blue, S. B. Bayram, and S. D. Marcum, "Creating, implementing, and sustaining an advanced optical spectrscopy laboratory course," Am. J. Phys. **78**, 503–509 (2010).

[7] B. L. Sands, M. J. Welsh, S. Kin, R. Marhatta, J. D. Hinkle, and S. B. Bayram, "Raman scattering spectroscopy of liquid nitrogen molecules: An advanced undergraduate physics laboratory experiment," Am. J. Phys. **75**, 488–495 (2007).

[8] G. Herzberg, *Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules*, 2nd. ed. (D. Van Nostrand Co., Princeton, NJ, 1950).

[9] H. Bock and P. D. Mollère, "Photoelectron spectra: An experimental approach to teaching molecular orbital models," J. Chem. Educ. **51**, 506–514 (1974).

[10] A. Lofthus and P. H. Krupenie, "The spectrum of molecular nitrogen," J. Phys. Chem. Ref. Data **6**, 113–307 (1977).

[11] N. K. Bibinov, A. A. Fateev, and K. Wiesemann, "On the influence of metastable reactions on rotational temperatures in dielectric barrier discharges in He-N_2 mixtures," J. Phys. D **34**, 1819–1826 (2001).

[12] A. Bogaerts and G. Renaat, "Similarities and differences between direct current and radio-frequency glow discharges: a mathematical simulation," J. Anal. At. Spectrom. **15**, 1191–1201 (2000).

[13] A. Qayyum, Z. Shaista, M. A. Naveed, N. U. Rehman, S. A. Ghauri, and M. Zakaullah, "Optical emission spectroscopy of Ar-N_2 mixture plasma," J. Quant. Spectrosc. Radiat. Transf. **107**, 361–371 (2007).

[14] A. A. Radzig and B. M. Smirnov, *Reference Data on Atoms, Molecules and Ions* (Springer-Verlag, Berlin, 1985).

[15] R. R. Laher and F. R. Gilmore, "Improved fits for the vibrational and rotational constants of many states of nitrogen and oxygen," J. Phys. Chem. Ref. Data. **20**, 685–712 (1991).

[16] P. M. Morse, "Diatomic molecules according to the Wave Mechanics. II. Vibrational Levels," Phys. Rev. **34**, 57–74 (1929).

[17] L. Lessinger, "Morse oscillators, Birge-Sponer extrapolation, and the electronic absorption spectrum of I_2," J. Chem. Educ. **71**, 388–391 (1994).

[18] C. J. Pursell and L. Doezema, "The electronic absorption spectrum of molecular iodine: A new fitting procedure for the physical chemistry laboratory," J. Chem. Educ. **76**, 839–841 (1999).

[19] R. T. Birge and H. Sponer, "The heat of dissociation of non-polar molecules," Phys. Rev. **28**, 259–283 (1926).

[20] R. Knight, *Physics for Scientists and Engineers*, 2nd. ed. (Pearson Education, Inc., San Francisco, CA, 2008).