

## VIBRATIONAL STRUCTURE OF RESONANCE RAMAN SPECTRA \*

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The intensity distribution of vibrational progressions in resonance Raman spectra is studied on a simple model. Expressions are derived for the dependence of this vibrational structure on the wavelength of the incident light and on temperature.

One of the most striking features of resonance Raman (RR) spectra in comparison to ordinary Raman spectra is the presence of prominent vibrational progressions [1]. The first attempts [2,3] to account for the overtones were based solely on the resonance terms in the perturbation description, but this turned out to be quantitatively unsatisfactory [4]. Subsequently Jacon et al. [4] showed that off-resonance terms, in particular the near-resonance terms associated with levels close to the resonance levels, contribute on a par with resonance terms. They demonstrated by direct computation that the inclusion of both terms accurately reproduces the intensities of the first overtones ( $\Delta v = 2$ ) relative to the fundamentals ( $\Delta v = 1$ ) in the RR spectra of  $I_2$  obtained with the 7 suitable lines of the argon ion laser [4].

To understand intensity distributions in RR progressions in a general way it seems useful to start from the analogy with intensity distributions in absorption and emission, which are well-known to be governed by the Franck-Condon principle. In this note we study the RR analog of this principle for simple model potentials. Similar studies applied to absorption and emission spectra have been very helpful in the early days of molecular electronic spectroscopy [5]. Since the vibrational integrals of RR spectra are more complicated than the Franck-Condon

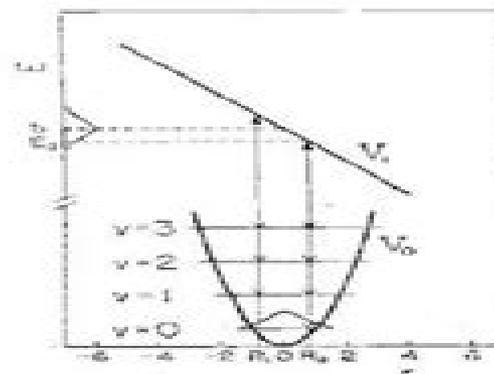


Fig. 1. Model potentials used to derive analytic expressions for resonance Raman intensity (divided by  $\omega^4$ ) distributions.

factors of absorption and emission bands, only the simplest models are expected to be amenable to analytic solution.

The model adopted is illustrated in fig. 1. It consists of an isolated diatomic molecule with a harmonic ground-state potential  $V_0$  and a linear repulsive excited state potential  $V_1$ .

\* Based on NRCC No. 13449.

† NRCC Postdoctoral Fellow 1972 - present.

# Chapter X Vibrational Spectra And Structure Of 2

**SA Adler**



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### **Table of Contents Chapter X Vibrational Spectra And Structure Of 2**

1. Understanding the eBook Chapter X Vibrational Spectra And Structure Of 2
  - The Rise of Digital Reading Chapter X Vibrational Spectra And Structure Of 2
  - Advantages of eBooks Over Traditional Books
2. Identifying Chapter X Vibrational Spectra And Structure Of 2
  - Exploring Different Genres
  - Considering Fiction vs. Non-Fiction
  - Determining Your Reading Goals
3. Choosing the Right eBook Platform
  - Popular eBook Platforms
  - Features to Look for in an Chapter X Vibrational Spectra And Structure Of 2
  - User-Friendly Interface
4. Exploring eBook Recommendations from Chapter X Vibrational Spectra And Structure Of 2
  - Personalized Recommendations
  - Chapter X Vibrational Spectra And Structure Of 2 User Reviews and Ratings
  - Chapter X Vibrational Spectra And Structure Of 2 and Bestseller Lists

5. Accessing Chapter X Vibrational Spectra And Structure Of 2 Free and Paid eBooks
  - Chapter X Vibrational Spectra And Structure Of 2 Public Domain eBooks
  - Chapter X Vibrational Spectra And Structure Of 2 eBook Subscription Services
  - Chapter X Vibrational Spectra And Structure Of 2 Budget-Friendly Options
6. Navigating Chapter X Vibrational Spectra And Structure Of 2 eBook Formats
  - ePub, PDF, MOBI, and More
  - Chapter X Vibrational Spectra And Structure Of 2 Compatibility with Devices
  - Chapter X Vibrational Spectra And Structure Of 2 Enhanced eBook Features
7. Enhancing Your Reading Experience
  - Adjustable Fonts and Text Sizes of Chapter X Vibrational Spectra And Structure Of 2
  - Highlighting and Note-Taking Chapter X Vibrational Spectra And Structure Of 2
  - Interactive Elements Chapter X Vibrational Spectra And Structure Of 2
8. Staying Engaged with Chapter X Vibrational Spectra And Structure Of 2
  - Joining Online Reading Communities
  - Participating in Virtual Book Clubs
  - Following Authors and Publishers Chapter X Vibrational Spectra And Structure Of 2
9. Balancing eBooks and Physical Books Chapter X Vibrational Spectra And Structure Of 2
  - Benefits of a Digital Library
  - Creating a Diverse Reading Collection Chapter X Vibrational Spectra And Structure Of 2
10. Overcoming Reading Challenges
  - Dealing with Digital Eye Strain
  - Minimizing Distractions
  - Managing Screen Time
11. Cultivating a Reading Routine Chapter X Vibrational Spectra And Structure Of 2
  - Setting Reading Goals Chapter X Vibrational Spectra And Structure Of 2
  - Carving Out Dedicated Reading Time
12. Sourcing Reliable Information of Chapter X Vibrational Spectra And Structure Of 2
  - Fact-Checking eBook Content of Chapter X Vibrational Spectra And Structure Of 2
  - Distinguishing Credible Sources
13. Promoting Lifelong Learning

- Utilizing eBooks for Skill Development
  - Exploring Educational eBooks
14. Embracing eBook Trends
- Integration of Multimedia Elements
  - Interactive and Gamified eBooks

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