Parameterized optical properties of monolayer MoSe$_2$

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Cite as: AIP Advances 9, 125132 (2019); doi: 10.1063/1.5125973
Submitted: 28 August 2019 • Accepted: 4 December 2019 • Published Online: 23 December 2019

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ABSTRACT
We report a model dielectric function, \( \varepsilon = \varepsilon_1 + i\varepsilon_2 \), of MoSe₂ from 1 to 6.42 eV with which the optical property of a MoSe₂ monolayer can be calculated at arbitrary temperatures from 31 to 300 K for potential application for device designs based on this material. Analytic representations, performed with the dielectric-function parametric model, allow interpolation with respect to both energy and temperature. We used reported spectrum data [Park et al., Sci. Rep. 8(1), 3173 (2018)] as the basis of our approach, verifying that the parameterized model dielectric function can reproduce the experimental data at various temperatures and can also produce the dielectric function (and the refractive index) at arbitrary temperatures.

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I. INTRODUCTION

Like many transition metal dichalcogenides (TMDCs), molybdenum diselenide (MoSe₂) has a layered structure of strong in-plane bonding and weak out-of-plane interactions. Because of these interactions, exfoliation is possible to realize two-dimensional layers of one unit cell thickness. MoSe₂ is well known as a TMDC that is a potential substitute for silicon or organic semiconductors in high-technology transistors, sensors, waveguides, and photodetectors.¹–⁷ Dielectric functions, \( \varepsilon = \varepsilon_1 + i\varepsilon_2 \), of MoSe₂, including temperature dependence, are needed to design devices for these applications. As a result, several researchers reported the dielectric function of a MoSe₂ monolayer at low temperatures and room temperature by using spectroscopic ellipsometry (SE).⁸–¹⁰ However, in order to be applied properly for device applications, the dielectric function of the monolayer MoSe₂ should be available at arbitrary temperatures. We note that the surface current model was applied to obtain optical properties of monolayers (and ultrathin films with some atomic layer thickness).¹¹ However, the purpose of this work is not to extract dielectric function values from experimental data but to utilize previously reported dielectric function spectra for further modeling to get optical properties at arbitrary temperatures.

Here, we meet this need by determining an analytic representation of \( \varepsilon \) of MoSe₂ over the energy range of 1–6.42 eV for temperatures from 31 to 300 K. We chose the experimental data published in Ref. 7 as the starting point since it covers a broad range of both spectrum and temperature, where obtaining critical-point (CP) energies was pursued from derivative spectra. The purpose of the current work is to reconstruct the original \( \varepsilon \) spectrum at arbitrary temperatures.

We follow the same approach applied for obtaining the dielectric function of the MoSe₂ monolayer and the InP bulk sample at any arbitrary temperature. It could also be applied to get optical properties of InAlAs and InAsSb alloys at arbitrary compositions, to mention a few. In brief, to represent basic asymmetric features of \( \varepsilon \), we used a dielectric-function parametric model (DFPM) that describes \( \varepsilon \) as a sum of asymmetric oscillators.¹²–¹⁴ In this work, the parameters were extracted by fitting the reported spectra with 11 dispersive oscillators and a pole
at each datum. Obtained model parameters at each temperature were fit to polynomials for achieving their temperature dependence to determine the optical properties of MoSe$_2$ at any temperature. These optical property values can be useful in designing devices based on this material and also in optical monitoring of the growth.

II. MODELING

The dielectric function spectrum in the DFPM is described as the sum of $m$ energy-bounded polynomials within the accessible spectral range and $P$ poles that represent outside contributions. The general expression is

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) = 1 + i \sum_{j=1}^{m} \frac{W_j(E)\Phi(h\omega, E, \sigma_j)}{E - E_j} + \sum_{j=m+1}^{m+P+1} \frac{A_j}{(h\omega)^2 - E_j^2},$$

(1)

where $W_j(E)$ is the joint density of states of the $j$th CP, and $\Phi$ is a function to describe the broadening which is usually with either a Lorentzian or Gaussian function. The detailed explanation with a calculation program of the DFPM is given in Refs. 14 and 15.

Figure 1 shows the description of each CP by nine parameters. All the parameters are well defined in Refs. 14 and 15, but, in brief, $E_C$ is the CP energy with $E_L$ and $E_U$ as its end points. $E_{LM}$ and $E_{UM}$ play an important role in controlling asymmetric characteristics of the CP structure. For energy regions (I, IV) and (II, III), the second- and fourth-order polynomials were used to construct the structure of the CP, respectively. The real part of $\varepsilon$ is calculated by a Kramers-Kronig relation.

III. RESULTS AND DISCUSSION

Figure 2 shows the reported dielectric function data of the MoSe$_2$ monolayer but with more number of spectra with a smaller temperature interval. Figures 2(a) and 2(b) are real and imaginary parts of dielectric functions, respectively, and the critical point identification is also borrowed from Ref. 7. To clarify the temperature dependence of the dielectric functions, an offset of 10 is added to every spectrum relative to that for temperature at 31 K.

Figure 3 shows the reconstructed $\varepsilon_2$ spectrum of MoSe$_2$ at 31 K, where data are open circles, and solid lines are the best fit for the
DFPM, which is obtained by the WVASE software (J. A. Woollam Co.) with respect to these data. The contributions from each component CP are well shown by the dashed lines. We reduced the number of data points appropriately to ensure fitting quality. We could successfully reconstruct the spectrum with only 11 CPs. We note that 12 CPs were reported in Ref. 7 where the 2nd derivative spectrum enhanced the resolution of the CP structures. However, this work of dealing only original nonderivative spectra could not resolve small E and F CP structures whose energy difference is predicted to be only about 0.3 eV.16

To obtain ε values for arbitrary temperatures, we used a third-order polynomial equation,

\[ f(x) = a + bx + cx^2 + dx^3 \]  

(2)
to fit all parameters in Table I. The best-fit parameters are shown in Table II. With these parameter values, we can obtain dielectric functions for arbitrary temperatures from 31 to 300 K.

Figure 4 shows temperature dependence of \( E_c \) parameter values. The open dots show parameter values at each reported temperature with the solid lines as the best fits to Eq. (2). Blue shifts of all \( E_c \) parameters which represent the CP energy positions in the DFPM are shown, which can be explained phenomenologically by reduced electron-phonon interaction and a reduced lattice constant at low temperatures.17 However, it should be emphasized that this \( E_c \) value is a parameter to construct dielectric function spectrum values at arbitrary temperatures and not to obtain CP energy values from the measured dielectric function spectrum. For the latter purpose, the 2nd derivative method of the spectrum is traditionally used, and precise CP energy values with their temperature dependence are reported in detail in Ref. 7.

### Table I. Fitted parameter values of the DFPM for MoSe\(_2\) at 31 K. Fixed value parameters are shown with asterisks.

| CP | No. | \( C_L \) | \( C_U \) | \( E_C \) (eV) | \( A \) | \( \Gamma \) (meV) | \( E_{LM} \) | \( A_{LM} \) | \( E_{UM} \) | \( A_{UM} \) |
|----|-----|---------|---------|--------------|-------|--------------|---------|-------------|--------|-------------|
| \( E_0 \) | 0   |         |         | 1.52         |       |              |         |             |        |             |
| A-  | 1   | 0       | 2       | 1.61         | 28.85 | 19*          | 0.688* | 0.01*       | 0.9*  | 0.406*      |
| A   | 2   | 0       | 3       | 1.66         | 43.99 | 14.36        | 0.63*  | 0.07*       | 0.98* | 0.095       |
| B   | 3   | 2       | 4       | 1.85         | 23.49 | 15.91        | 0.067* | 0.01*       | 0.7*  | 0.177       |
| \( C_A \) | 4   | 3       | 6       | 2.47         | 10.65 | 67.75        | 0.15*  | 0.07*       | 0.9*  | 0.01*       |
| \( C_B \) | 5   | 3       | 6       | 2.62         | 87.08 | 138.03       | 0.84*  | 0.188*      | 0.7*  | 0.224*      |
| E and F | 6   | 5       | 8       | 3.41         | 65.87 | 217.18       | 0.84*  | 0.197*      | 0.77* | 0.128*      |
| \( E_1 \) | 7   | 6       | 10      | 3.60         | 11.96 | 54.79        | 0.208* | 0.1*        | 0.952*| 0.239*      |
| \( E_2 \) | 8   | 6       | 10      | 3.75         | 20.76 | 128.88       | 0.036* | 0.01*       | 0.368*| 0.167*      |
| \( E_3 \) | 9   | 7       | 11      | 4.20         | 8.29  | 122.41       | 0.011* | 0.01*       | 0.9*  | 0.107*      |
| \( E_4 \) | 10  | 7       | 11      | 4.35         | 16.97 | 129.75       | 0.9*   | 0.593*      | 0.7*  | 0.557*      |
| \( E_5 \) | 11  | 10      | 12      | 6.12*        | 8.92  | 230*         | 0.57*  | 0.393*      | 0.9*  | 0.463       |
| \( E_6 \) | 12  |         |         | 25.22        |       |              |         |             |        |             |
| Pole |     |         |         | 0.01*        | 6.6*  |              |         |             |        |             |
TABLE II. Parameter values obtained by fitting with Eq. (2) for temperature dependence.

|       | a    | b    | c    | d    |
|-------|------|------|------|------|
| $E_0$ | 1.516| 0.384| -4.919| 8.865|
| A     | 1.614| -0.080| -0.882| 0    |
| A     | 1.665| -0.144| -0.583| 0    |
| B     | 1.853| -0.029| -1.840| 3.446|
| $C_0$ | 2.480| -0.236| -0.493| 0    |
| $C_0$ | 2.628| -0.103| -0.784| 0    |
| E and F | 3.409| 0.116| -0.656| 0    |
| $E_1$ | 3.605| -0.101| -0.757| 0    |
| $E_2$ | 3.762| -0.119| -0.158| 0    |
| $E_3$ | 4.221| -0.382| 0.891| 0    |
| $E_4$ | 4.375| -0.477| 1.268| 0    |
| $E_5$ | 23.873| 52.2| -521.32| 873.77|
| $A_1 (A)$ | 27.38| 91.90| -1291.4| 2327.3|
| $A_2 (A)$ | 42.12| 60.00| -1291.4| 2327.3|
| $A_3 (A)$ | 21.45| 76.90| -564.17| 828.39|
| $A_4 (A)$ | 11.47| -15.80| -12.78| 0    |
| $A_5 (A)$ | 84.17| -0.144| -0.583| 0    |
| $E_1 (A_1)$ | 64.76| 23.60| 13.99| 0    |
| $E_1 (A_2)$ | 12.12| -4.14| 5.60| 0    |
| $E_1 (A_3)$ | 20.12| 21.60| -161.81| 230.1|
| $E_1 (A_4)$ | 8.40| -6.49| 66.01| -142.8|
| $E_1 (A_5)$ | 16.61| 8.42| -27.93| 0    |
| $E_1 (A_6)$ | 8.80| 4.02| -13.97| 0    |

Figure 5 compares the reported original experimental data (black dashed lines) to the final reconstruction of this work (gray solid lines) at 31 and 250 K. The reconstructions agree well with the data on this scale along with a slight discrepancy near 1.5–2.5 eV in $\varepsilon_1$. However, the overall agreement supports the validity of our work. We can now calculate both real and imaginary parts of $\varepsilon$ of MoSe$_2$ for any arbitrary temperature, as shown in Figs. 6(a) and 6(b), respectively. The spectra are offset by increments of 15 relative to that for 40 K. Careful comparison shows that noise can be well observed, as shown in Fig. 2, of experimental data, while no noise exists in the constructed model values, as shown in Fig. 6.
FIG. 6. Constructed complex dielectric functions, \( \varepsilon = \varepsilon_1(a) + i\varepsilon_2(b) \), of MoSe\(_2\) at arbitrary temperatures by the parameters given in Tables I and II.

IV. SUMMARY AND CONCLUSIONS

We obtain a model dielectric function of the MoSe\(_2\) monolayer in a spectral range of 1–6.42 eV for a temperature range of 31–300 K. The DFPM successfully describes the data with 11 physically meaningful CPs including the sharp trionic feature \( A^- \). The temperature dependence of the necessary parameters was obtained by fitting the model parameters with 3rd order polynomial equations. Hence, dielectric functions of MoSe\(_2\) for continuous
temperatures are determined for a spectral range of 1.0–6.42 eV. We believe that these results will be useful especially in technological applications such as monitoring the growth and the design of MoSe₂ related devices.

ACKNOWLEDGMENTS

This work was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (Grant No. NRF-2016R1D1A1B03931421) and also supported by the NRF grant funded by the Korean government (MSIP) (Grant No. NRF-2016R1A2B1013734).

REFERENCES

1 S. R. Das, J. Kwon, A. Prakash, C. J. Delker, S. Das, and D. B. Janes, Appl. Phys. Lett. 106, 083507 (2015).
2 F. Hu, Y. Luan, M. E. Scott, J. Yan, D. G. Mandrus, X. Xu, and Z. Fei, Nat. Photonics 11, 356 (2017).
3 Y.-H. Chang, W. Zhang, Y. Zhu, Y. Han, J. Pu, J.-K. Chang, W.-T. Hsu, J.-K. Huang, C.-L. Hsu, M.-H. Chiu, T. Takenobu, H. Li, C.-I. Wu, W.-H. Chang, A.-T. S. Wee, and L.-J. Li, ACS Nano 8, 8582 (2014).
4 I. Abid, W. Chen, J. Yuan, A. Bohloul, S. Najmaei, C. Avendano, R. Péchou, A. Mayyah, and J. Lou, ACS Photonics 4, 1653 (2017).
5 H.-L. Liu, C.-C. Shen, S.-H. Su, C.-L. Hsu, M.-Y. Li, and L.-J. Li, Appl. Phys. Lett. 105, 201905 (2014).
6 B. K. Choi, M. Kim, K.-H. Jung, J. Kim, K.-S. Yu, and Y. J. Chang, Nanoscale Res. Lett. 12, 492 (2017).
7 H. G. Park, T. J. Kim, F. Ullah, V. L. Le, H. T. Nguyen, Y. S. Kim, and Y. D. Kim, Sci. Rep. 8(1), 3173 (2018).
8 Y. Li and T. F. Heinz, 2D Mater. 5, 025021 (2018).
9 Y. L. Le, T. J. Kim, H. G. Park, H. T. Nguyen, X. A. Nguyen, and Y. D. Kim, Curr. Appl. Phys. 19, 182 (2019).
10 T. J. Kim, S. Y. Hwang, J. S. Byun, M. S. Diware, J. Choi, H. G. Park, and Y. D. Kim, J. Appl. Phys. 112, 013505 (2012).
11 T. J. Kim, J. C. Park, N. S. Barange, H. G. Park, Y. R. Kang, K. H. Nam, and Y. D. Kim, Curr. Appl. Phys. 15, 530 (2015).
12 S. Y. Hwang, T. J. Kim, S. S. Byun, N. S. Barange, M. S. Diware, Y. D. Kim, D. E. Aspnes, J. J. Yoon, and J. D. Song, Thin Solid Films 547, 276 (2013).
13 M. Cardona, Modulation Spectroscopy (Academic Press, 1969).
14 B. Johs, C. M. Herzinger, J. H. Dinan, A. Cornfeld, and J. D. Benson, Thin Solid Films 313, 137 (1998).
15 C. M. Herzinger and B. D. Johs, U.S. Patent 5,796,983 (14 August 1995).
16 R. Gillen and J. Maultzsch, IEEE J. Sel. Top. Quantum Electron. 23, 219 (2017).
17 S. Gopalan, P. Lautenschlager, and M. Cardona, Phys. Rev. B 35, 5577 (1987).